10-30-2009

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Accepted version. *Organometallics*, Vol. 28, No. 22 (October 30, 2009): 6585-6592. DOI. © 2009 American Chemical Society. Used with permission.

Scope and Mechanistic Investigations on the Solvent-Controlled Regio- and Stereoselective Formation of Enol Esters from the Ruthenium-Catalyzed Coupling Reaction of Terminal Alkynes and Carboxylic Acids

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Abstract: The ruthenium-hydride complex $(PCy_3)_2(CO)RuHCl$ was found to be a highly effective catalyst for the alkyne-to-carboxylic acid coupling reaction to give synthetically useful enol ester products. Strong solvent effect was observed for the ruthenium catalyst in modulating the activity and selectivity; the coupling reaction in CH_2Cl_2 led to the regioselective formation of *gem*-enol ester products, while the stereoselective formation of (*Z*)-enol esters was obtained in THF. The coupling reaction was found to be strongly inhibited by PCy_3. The coupling reaction of both $PhCO_2H/PhC{\equiv}CD$ and $PhCO_2D/PhC{\equiv}CH$ led to the extensive deuterium incorporation on the vinyl positions of the enol ester products. An opposite Hammett value was observed when the correlation of a series of *para*-substituted p-X-$C_6H_4CO_2H$ (X = OMe, CH_3, H, CF_3, CN) with phenylacetylene was examined in $CDCl_3$ ($\rho = +0.30$) and THF ($\rho = -0.68$). Catalytically relevant Ru-carboxylate and −vinylidene-carboxylate complexes, $(PCy_3)_2(CO)(Cl)Ru(\kappa^2\text{-}O_2CC_6H_4\text{-}p\text{-}OMe)$ and $(PCy_3)_2(CO)(Cl)RuC(=CHPh)O_2CC_6H_4\text{-}p\text{-}OMe$, were isolated, and the structure of both complexes was completely established by X-ray crystallography. A detailed mechanism of the coupling reaction involving a rate-limiting C-O bond formation step was proposed on the basis of these kinetic and structural studies. The regioselective formation of the *gem*-enol ester products in CH_2Cl_2 was rationalized by a direct migratory insertion of the terminal alkyne via a Ru-carboxylate species, whereas the stereoselective formation of (*Z*)-enol ester products in THF was explained by invoking a Ru-vinylidene species.

Introduction

Enol esters are a versatile class of precursors for a variety of synthetically important organic transformations such as cycloaddition,[1] asymmetric hydrogenation,[2] C-C bond coupling,[3] and Aldol- and Mannich-type of condensation reactions.[4] Since enol esters can also serve as a synthon for aldehydes and ketones, much research efforts has been devoted to develop efficient catalytic methods to control both regio- and stereoselectivity in forming substituted enol esters. Notable recent examples on the catalytic synthesis of enol esters include: Zr-catalyzed methylalumination of alkynes,[5] Au-catalyzed intramolecular rearrangements of propargylic esters and alcohols,[6] Cu-catalyzed oxidative esterification of aldehydes with β-dicarbonyl compounds,[7] and asymmetric coupling reaction of ketenes with aldehydes by chiral Fe catalysts.[8] From an industrial perspective of increasing synthetic efficiency as well as for reducing waste byproducts, catalytic methods for producing enol esters are highly desired compared to the classical methods that utilize stoichiometric amounts of strong base or toxic Hg salts.[9]

Transition metal-catalyzed alkyne-to-carboxylic acid coupling reaction offers an attractive route to enol esters, but its synthetic potential has not been fully exploited in part because the catalytic method typically produces a mixture of *gem*- and (*E*)/(*Z*)-enol ester products.[10] Considerable research has been devoted to control both regio- and stereoselectivity of the enol ester products by modulating steric and electronic nature of the metal catalysts. Generally, late transition metal catalysts have been found to be effective for producing a mixture of (*E*)- and (*Z*)-enol esters from *anti*-Markovnikov addition of carboxylic acids to terminal alkynes over *gem*-enol ester products,[10,11] though the regioselective formation of *gem*-enol esters has been achieved by using Ru and Rh catalysts.[12] Dixneuf and co-workers elegantly showed the relationship between steric environment of the ruthenium-phosphine catalysts and the stereoselective formation of the (*Z*)-enol esters.[13] In a subsequent study, the same authors reported a regioselective 2:1 alkyne-to-carboxylic acid coupling reaction to form the dienyl esters by using Cp*Ru(COD)Cl catalyst, in which a ruthenacyclopentadiene complex was proposed as the key intermediate species for the coupling reaction.[14] Both intra- and intermolecular versions of the catalytic alkyne-to-carboxylic coupling methods have been successfully applied to the synthesis of complex organic molecules.[15] Despite considerable synthetic and mechanistic progress, however, neither the nature of reactive intermediate species nor controlling factors for the formation of *gem*- vs (*E*)/(*Z*)-enol esters has been clearly established.

We previously reported that the coordinatively unsaturated ruthenium-hydride complex $(PCy_3)_2(CO)RuHCl$ (**1**) is a highly effective catalyst for the coupling reactions of alkenes and alkynes.[16] Both ruthenium-acetylide and –vinylidene complexes have been found to be the key species for these coupling reactions.[17] As part of on-going efforts to extend synthetic utility of the ruthenium-catalyzed alkyne coupling reactions, we have been exploring the catalytic activity of the ruthenium-hydride complexes toward the coupling reactions of alkynes with heteroatom substrates. In this article, we report a detailed scope and mechanistic study of the ruthenium-catalyzed alkyne-to-carboxylic acid coupling reaction, which provides new insights in mediating solvent-controlled regio- and stereoselective formation of the enol ester products.

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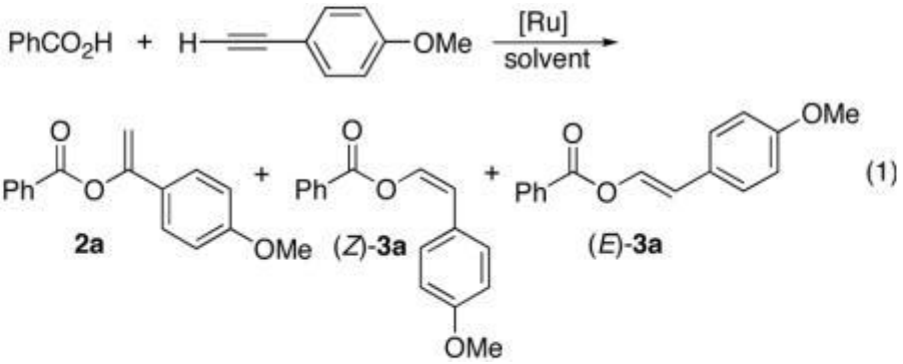

(1)

Results and Discussion

Catalyst Survey and Reaction Scope

The catalytic activity of selected ruthenium complexes was initially screened for the coupling reaction of benzoic acid and 4-ethynylanisole (eq 1). Among the selected ruthenium catalysts, complex **1** was found to exhibit uniquely high catalytic activity and selectivity in giving the *gem*-enol ester product **2a** within 5 h at 95 °C in CH_2Cl_2 (Table 1). Both $Ru_3(CO)_{12}$ and $Cp^*Ru(PPh_3)_2Cl$ showed significant activity, but suffered from low selectivity in forming the coupling products. The catalyst Cp*Ru(COD)Cl, on the other hand, produced a mixture of 1:1 and 1:2 coupling products, which is in line with the previously reported results on the formation of dienyl ester products.[14]

Table 1. Catalyst Survey on the Coupling Reaction of Benzoic Acid and 4-Ethynylanisole.[a]

entry	catalyst	yield (%)[b]	2a:(*Z*)-3a:(*E*)-3a
1	$(PCy_3)_2(CO)RuHCl$ (**1**)	>95	100:0:0
2	$(PPh_3)_3(CO)RuH_2$	0	
3	$(PPh_3)_3RuCl_2$	0	
4	$(PPh_3)_3RuHCl$	0	
5	$RuCl_3 \cdot 3H_2O$	0	
6	$[RuCl_2(COD)]_x$	0	
7	$Ru_3(CO)_{12}$	90	8:17:75
8	$Cp^*Ru(PPh_3)_2Cl$	50	15:50:35
9	Cp*Ru(COD)Cl	60	22:78[c]

[a]Reaction conditions: benzoic acid (0.10 mmol), 4-ethynylanisole (0.15 mmol), catalyst (2 mol %), CH_2Cl_2 (2 mL), 95 °C, 8 h.

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[b]GC yields based on benzoic acid.
[c]The ratio of **2a** and 1:2 coupling products.

Next, the solvent effect on the activity and selectivity patterns of the catalyst was examined for the coupling reaction of benzoic acid and 4-ethynylanisole (Table 2). A remarkably strong solvent influence on the ruthenium catalyst **1** was observed in modulating the formation of the enol ester products. Thus, the coupling reaction in relatively non-polar and non-coordinating solvents tended to favor the formation of geminal coupling product **2a** over (*E*)- and (*Z*)-**3a**, of which CH_2Cl_2 was found to be the best in producing the geminal product **2a** among these solvents (entry 4). In contrast, among polar coordinating solvents, which tended to favor the formation of (*Z*)-enol ester product (*Z*)-**3a**, THF was found to be the most selective in giving (*Z*)-**3a** (entry 10). It should be emphasized that the formation of 1:2 coupling products was not observed from the coupling reaction catalyzed by **1**. Other ruthenium catalysts such as $Ru_3(CO)_{12}$, $Cp^*Ru(PPh_3)_2Cl$ and $Cp^*Ru(COD)Cl$ surveyed in Table 1 did not exhibit similar degree of solvent control in forming the coupling products.

Table 2. Solvent Effect on the Coupling Reaction of Benzoic Acid and 4-Ethynylanisole Catalyzed by 1.[a]

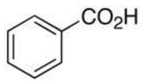
entry	**solvent**	**2a:(*Z*)-3a:(*E*)-3a**	**yield (%)[b]**
1	benzene	51:40:9	80
2	toluene	68:26:6	70
3	*n*-hexane	71:18:11	75
4	**CH_2Cl_2**	**99:1:0**	>**99**
5	Et_2O	13:20:67	60
6	CH_3CN	33:55:13	55
7	DME	5:74:21	50
8	DMSO	2:48:50	53
9	H_2O	3:44:53	73
10	**THF**	**0:100:0**	>**99**

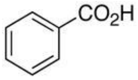
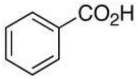
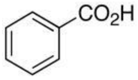
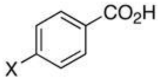
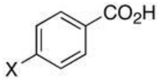
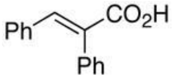
[a]Reaction conditions: benzoic acid (0.10 mmol), 4-ethynylanisole (0.15 mmol), **1** (14 mg, 2 mol %), solvent (2 mL), 95 °C, 8 h.
[b]GC yields based on benzoic acid.

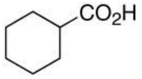
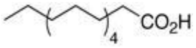
It is imperative to briefly mention about the recent advances in using solvents with different polarity and coordinating ability to control the product selectivity. Coordinatively unsaturated transition metal complexes have been found to be particularly sensitive to the nature of solvents in mediating unreactive bond activation reactions.[18–20] For example, Milstein discovered a remarkable solvent effect of the pincer-ligated (PCP)Rh complexes in directing C-H vs C-C bond and C-I vs C-CN bond activation reactions.[18] Jones investigated the similar solvent control effects in C-C vs C-H bond cleavage reactions of alkenyl nitriles by using well-defined Ni-diphosphine complexes.[19] The regioselectivity of a number of synthetically useful catalytic coupling reactions of alkenes and alkynes, such as Heck-type and allylic substitution reactions, has also been successfully controlled by using different solvents.[20]

The scope of the coupling reaction was surveyed in both CH_2Cl_2 and THF by using the catalyst **1** (Table 3). Excellent degree of solvent-control was observed for the coupling reaction of terminal alkynes with carboxylic acids in facilitating regio- and stereoselective formation of the enol ester products. Thus, the coupling reaction in CH_2Cl_2 led to the exclusive formation of the *gem*-enol ester product **2** for both aliphatic and aryl-substituted terminal alkynes. In contrast, the coupling reaction for aryl-substituted alkynes in THF predominantly gave the (*Z*)-enol ester products (*Z*)-**3**. The electronic nature of the alkynes was found to be an important factor in dictating regioselective product formation, since *gem*-enol ester product **2** was formed predominantly with the aliphatic terminal alkynes, even when the reaction was performed in THF (entries 17–19, 32, 34). In all cases, a relatively low catalyst loading (1–2 mol %) was used for the coupling reaction, and the enol ester products were readily isolated in high yields after a simple column chromatography on silica gel.

Table 3. Alkyne-to-Carboxylic Acid Coupling Reaction.[a]

entry	acid	alkyne	solvent		product ratio (2:(*Z*)-3:(*E*)-3)	yd (%)[b]
1		$H{-}{\equiv}{-}C_6H_4$-*p*-R	**CH_2Cl_2**	R = OMe	**2a**:(*Z*)-**3a**:(*E*)-**3a** = 100:0:0	91
2				R = Me	**2b**:(*Z*)-**3b**:(*E*)-**3b** = 100:0:0	87
3				R = H	**2c**:(*Z*)-**3c**:(*E*)-**3c** = 100:0:0	98
4				R = Br	**2d**:(*Z*)-**3d**:(*E*)-**3d** = 100:0:0	89
5				R = CF_3	**2e**:(*Z*)-**3e**:(*E*)-**3e** = 100:0:0	90
6				R = F	**2f**:(*Z*)-**3f**:(*E*)-**3f** = 100:0:0	87
7		$H{-}{\equiv}{-}C_6H_4$-*p*-R	**THF**	R = OMe	**2a**:(*Z*)-**3a**:(*E*)-**3a** = 0:100:0	95

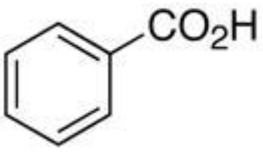
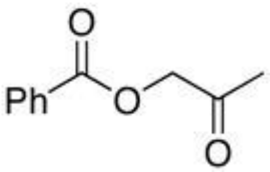
entry	**acid**	**alkyne**	**solvent**		**product ratio (2:(*Z*)-3:(*E*)-3)**	**yd (%)**[b]
8				R = Me	**2b**:(*Z*)-**3b**:(*E*)-**3b** = 0:86:14	90
9				R = H	**2c**:(*Z*)-**3c**:(*E*)-**3c** = 0:87:13	98
10				R = Br	**2d**:(*Z*)-**3d**:(*E*)-**3d** = 0:94:6	89
11				R = CF_3	**2e**:(*Z*)-**3e**:(*E*)-**3e** = 0:93:7	90
12				R = F	**2f**:(*Z*)-**3f**:(*E*)-**3f** = 0:90:10	87
13		1-hexyne	**CH_2Cl_2**		**2g**:(*Z*)-**3g**:(*E*)-**3g** = 100:0:0	97
14		$HCCCH_2Ph$			**2h**:(*Z*)-**3h**:(*E*)-**3h** = 100:0:0	96
15		3-methyl-3-buten-1-yne			**2i**:(*Z*)-**3i**:(*E*)-**3i** = 100:0:0	97
16		2-ethynyl-6-methoxynaphthalene			**2j**:(*Z*)-**3j**:(*E*)-**3j** = 100:0:0	87
17		1-hexyne	**THF**		**2g**:(*Z*)-**3g**:(*E*)-**3g** = 100:0:0	97
18		$HCCCH_2Ph$			**2h**:(*Z*)-**3h**:(*E*)-**3h** = 100:0:0	96
19		3-methyl-3-buten-1-yne			**2i**:(*Z*)-**3i**:(*E*)-**3i** = 100:0:0	97
20		2-ethynyl-6-methoxynaphthalene			**2j**:(*Z*)-**3j**:(*E*)-**3j** = 0:100:0	89
21			**CH_2Cl_2**	X = OMe	**2k**:(*Z*)-**3k**:(*E*)-**3k** = 100:0:0	83
22				X = Me	**2l**:(*Z*)-**3l**:(*E*)-**3l** = 100:0:0	90
23				X = Br	**2m**:(*Z*)-**3m**:(*E*)-**3m**= 100:0:0	68
24				X = CN	**2n**:(*Z*)-**3n**:(*E*)-**3n** = 100:0:0	89
25				X = CF_3	**2o**:(*Z*)-**3o**:(*E*)-**3o** = 100:0:0	90
26			**THF**	X = OMe	**2k**:(*Z*)-**3k**:(*E*)-**3k** = 0:90:10	95
27				X = Me	**2l**:(*Z*)-**3l**:(*E*)-**3l** = 0:90:10	93
28				X = Br	**2m**:(*Z*)-**3m**:(*E*)-**3m** = 0:92:8	90
29				X = CN	**2n**:(*Z*)-**3n**:(*E*)-**3n** = 3:92:5	83
30				X = CF_3	**2o**:(*Z*)-**3o**:(*E*)-**3o** = 8:81:11	85
31			**CH_2Cl_2**		**2p**:(*Z*)-**3p**:(*E*)-**3p** = 100:0:0	90
32		1-hexyne			**2q**:(*Z*)-**3q**:(*E*)-**3q** = 100:0:0	93
33			**THF**		**2p**:(*Z*)-**3p**:(*E*)-**3p** = 3:92:5	97

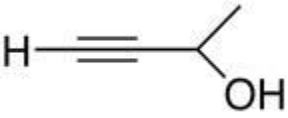
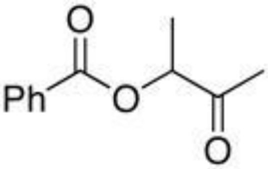
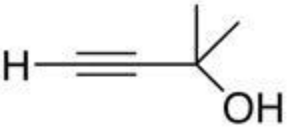
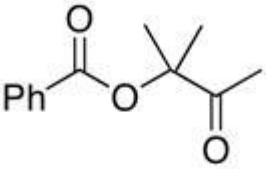
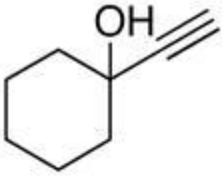
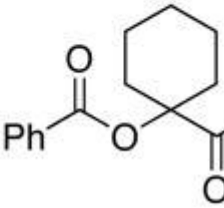
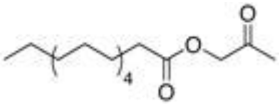
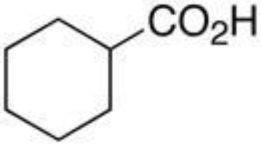
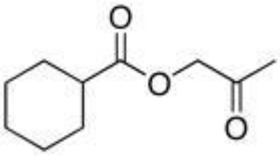
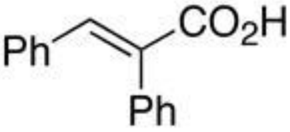
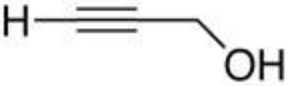
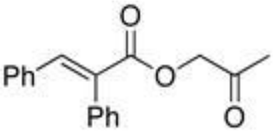
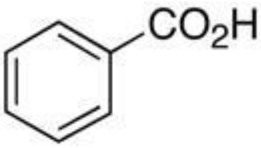
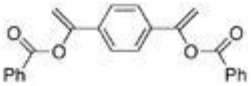
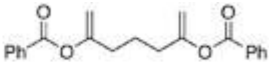
entry	**acid**	**alkyne**	**solvent**	**product ratio (2:(*Z*)-3:(*E*)-3)**	**yd (%)**[b]
34		1-hexyne		**2q**:(*Z*)-**3q**:(*E*)-**3q** = 100:0:0	96
35		H—≡—Ph	CH_2Cl_2	**2r**:(*Z*)-**3r**:(*E*)-**3r** = 88:12:0	90
36			**THF**	**2r**:(*Z*)-**3r**:(*E*)-**3r** = 0:93:7	93
37		H—≡—Ph	CH_2Cl_2	**2s**:(*Z*)-**3s**:(*E*)-**3s** = 89:11:0	91
38			**THF**	**2s**:(*Z*)-**3s**:(*E*)-**3s** = 0:90:10	91

[a]Reaction conditions: acid (1.0 mmol), alkyne (2.0 mmol), **1** (14 mg, 2 mol %), solvent (2–3 mL), 90–95 °C, 8–12 h.
[b]Isolated yield.

To further demonstrate the synthetic efficacy of the ruthenium catalyst **1**, we next examined the coupling reaction of carboxylic acids with both propargylic alcohols and diynes (Table 4). The catalyst **1** was found to catalyze the coupling reaction of carboxylic acids with propargylic alcohols to give the acetomethyl ester products **4** in high yields. In these cases, exclusive formation of the ketone product was formed from the Markovnikov-selective hydration of the alkynes. Such Markovnikov-selectivity has been generally preferred for the hydration of terminal alkynes,[21] although *anti*-Markovnikov selective hydration of alkynes has been achieved more recently by using late transition metal catalysts.[22] The analogous coupling reaction with an aryl-substituted diyne 1,4-diethynylbenzene in CH_2Cl_2 predictably yielded the corresponding *gem*-dienol diester product **5a** (entry 8), while a mixture of *gem*-, (*E*)- and (*Z*)-dienol diester products was formed in THF (*gem*:(*E*):(*Z*) = 18:32:50, 91% combined yield). In contrast, an aliphatic diyne produced *gem*-dienol diester **5b** exclusively in both CH_2Cl_2 and THF (entry 9).

Table 4. Coupling Reaction of Carboxylic Acids with Propargylic Alcohols and Diynes.[a]

entry	**acid**	**alkyne**	**product(s)**	**yield (%)**[b]
1			 **4a**	98

entry	acid	alkyne	product(s)	yield (%)[b]
2			 **4b**	95
3			 **4c**	97
4			 **4d**	90
5			 **4e**	89
6			 **4f**	83
7			 **4g**	85
8[c]			 **5a**	90
9[c]				94

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entry	acid	alkyne	product(s)	yield (%)[b]
			5b	

[a] Reaction conditions: carboxylic acid (1.0 mmol), alkyne (2.0 mmol), **1** (14 mg, 2 mol %), CH_2Cl_2 (2–3 mL), 90–95 °C, 8–12 h.
[b] Isolated yield.
[c] 48 h of the reaction time.

Mechanistic Study: Phosphine Inhibition Study

The following experiments were performed to probe the factors influencing the formation of the enol ester products. First, the phosphine inhibition kinetics was measured from the coupling reaction of benzoic acid and phenylacetylene in the presence of the catalyst **1** (2 mol %). The plot of the initial rate (v_i), which was estimated from a first–order plot of *ln*[product] vs reaction time, as a function of [PCy_3] showed that the rate is inversely dependent on added [PCy_3] (Figure 1). The addition of PCy_3 (10–30 mM, 2.5–7.5 mol %) to the reaction mixture under otherwise similar conditions led to a steady decrease from $k_{obs} = 1.8 \times 10^{-2}$ h^{-1} (without added PCy_3) to 4.0×10^{-3} h^{-1} (30 mM of PCy_3). These results indicate that the active Ru catalyst is formed by a reversible dissociation of the phosphine ligand.

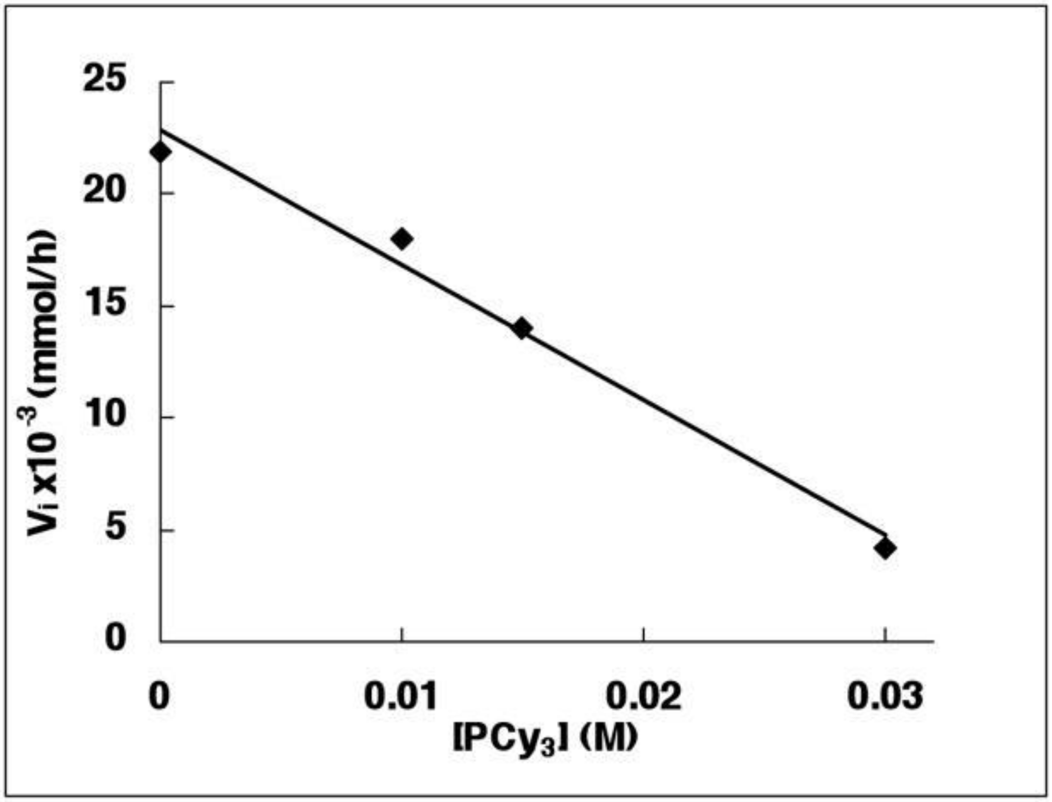

Figure 1. Plot of the Initial Rate (v_i) vs [PCy$_3$] for the Coupling Reaction of Benzoic Acid and Phenylacetylene.

Deuterium Labeling Study

The treatment of PhCO$_2$D with PhC≡CH (2.0 equiv) and **1** (2 mol %) in CH$_2$Cl$_2$ at 95 °C yielded the *gem*-enol ester product **2c** with ca. 30% D on both vinyl positions as determined by ^{1}H and ^{2}H NMR (Scheme 1). The analogous reaction in THF also formed the product (*Z*)-**3c** with a similar amount of deuterium on the vinyl positions. Conversely, the reaction of PhCO$_2$H with PhC≡CD (2 equiv) in CH$_2$Cl$_2$ and in THF formed the products, **2c** and (*Z*)-**3c** respectively, with nearly equal amounts of the deuterium (62–67%) on the vinyl positions. In a control experiment, the treatment of PhCO$_2$D with PhC≡CH (2.0 equiv) in the presence of **1** (2 mol %) led to almost complete H/D exchange within 10 min at 95 °C prior to the product formation. The ruthenium catalyst was found to be essential for the H/D exchange reaction, since no significant H/D exchange between PhCO$_2$D and PhC≡CH occurred in the absence of **1** under otherwise similar conditions. These results indicate that the H/D exchange

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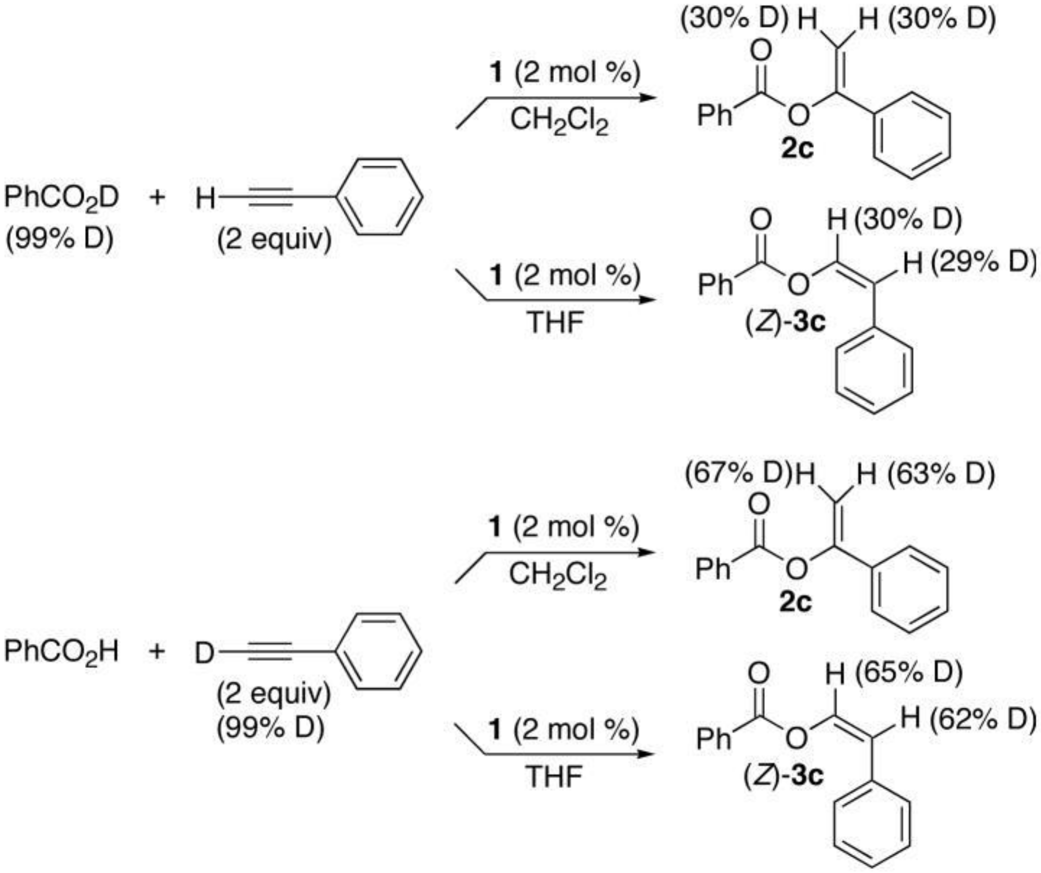
between the acid and alkynyl hydrogens is rapid and reversible, and that neither the alkynyl C–H bond nor the carboxylic acid O–H bond activation step is a rate-limiting step of the coupling reaction.



Scheme 1

Hammett Study

To discern the electronic effects on the product formation, the Hammett ρ values were measured for the coupling reaction in both $CDCl_3$ and THF. Thus, the correlation of relative rates with σ_p for a series of *para*-substituted benzoic acids p-X-$C_6H_4CO_2H$ (X = OMe, CH_3, H, CF_3, CN) with phenylacetylene in the presence **1** (2 mol %) at 95 °C led to the opposing trend between the reaction in $CDCl_3$ ($\rho = +0.30$) and in THF ($\rho = -0.68$) (Figure 2).[9b] An analogous correlation of the reaction rates of benzoic acid with a series of *para*-substituted alkynes p-Y-$C_6H_4C{\equiv}CH$ (Y = OMe, CH_3, H, F, CF_3) also resulted in the opposite slope between two solvents (ρ = −0.57 in $CDCl_3$ vs ρ = +0.33 in THF) (Figure 3).

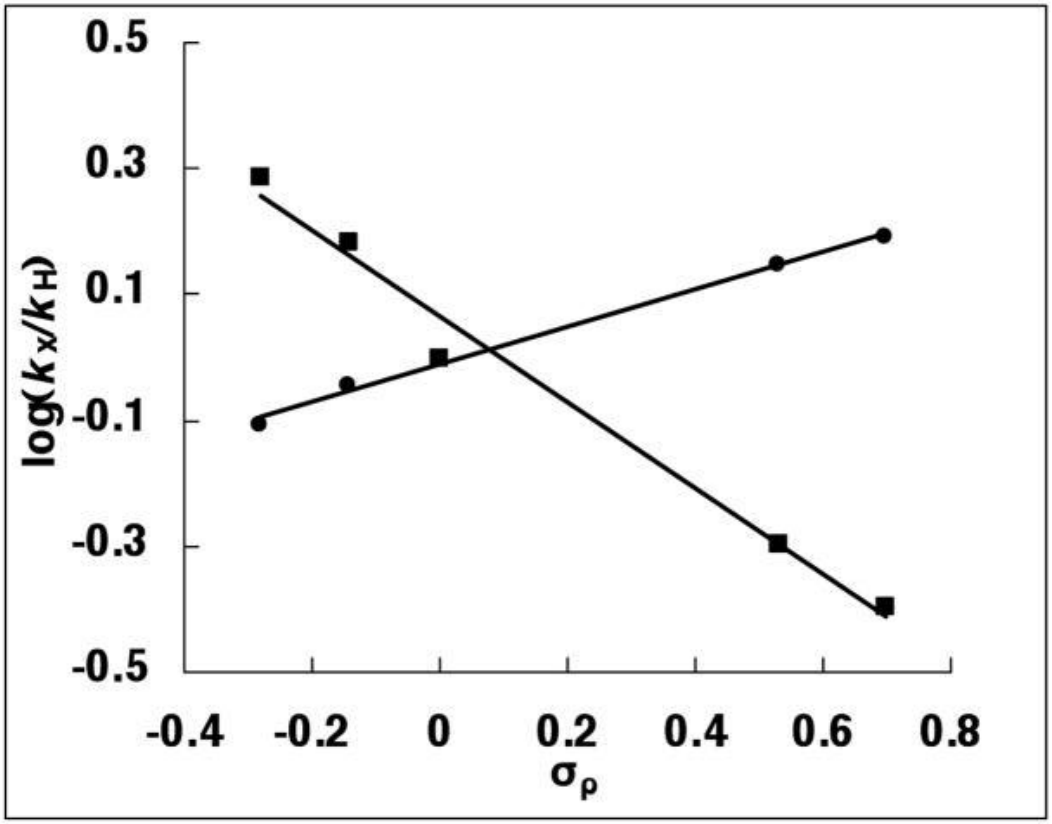


Figure 2. Hammett plots of the coupling reaction of *para*-substituted *p*-X-$C_6H_4CO_2H$ (X = OMe, CH_3, H, CF_3, CN) with phenylacetylene in $CDCl_3$ (●) and in THF (■).

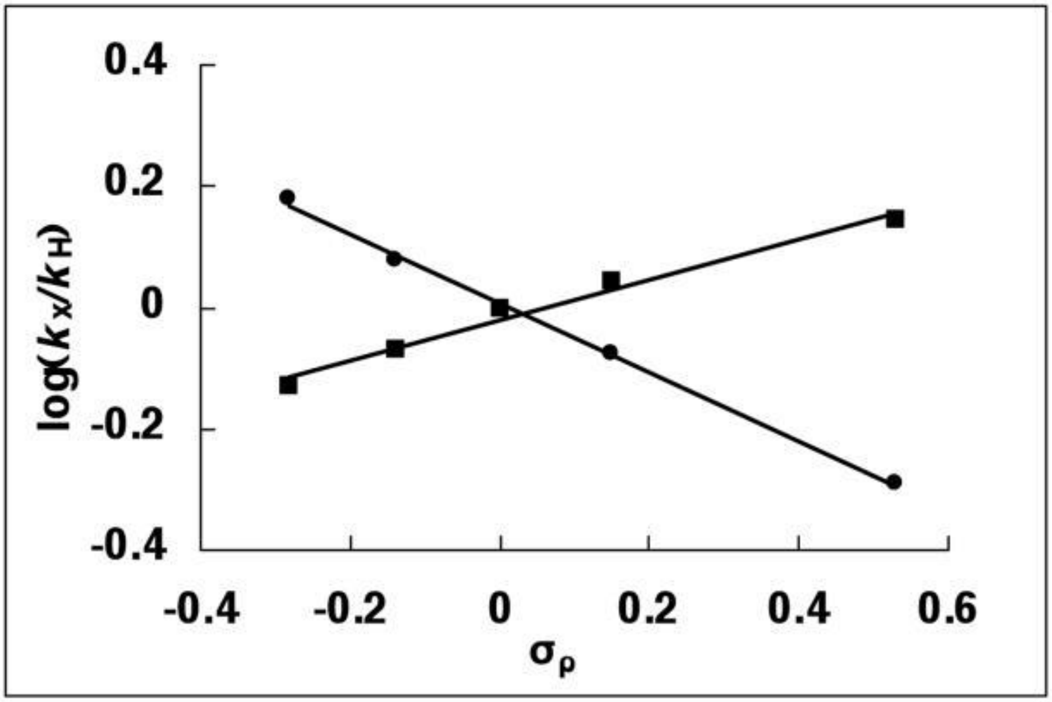


Figure 3. Hammett plots of the coupling reaction of benzoic acid with *para*-substituted *p*-Y-$C_6H_4C{\equiv}CH$ (Y = OMe, CH_3, H, F, CF_3) in $CDCl_3$ (●) and in THF (■).

The opposite Hammett ρ value indicates a different mechanistic pathway between the coupling reaction in $CDCl_3$ and in THF. The positive ρ value observed from the correlation of *para*-substituted benzoic acids *p*-X-$C_6H_4CO_2H$ in $CDCl_3$ matches well with a direct migratory insertion of the carboxylate group to a coordinated terminal alkyne, which is dictated by the nucleophilicity of a developing negative charge on the carboxylic oxygen. On the other hand, a negative ρ value obtained from the reaction in THF indicates considerable cationic character build-up on the transition state, and this can be explained via the formation of the Ru-vinylidene species, wherein electrophilic character of the α-vinylidene carbon has been well established.[10a,21a] The analogous opposite trend from the correlation of the alkynes *p*-Y-$C_6H_4C{\equiv}CH$ can similarly be rationalized in terms of developing a positive charge on the alkynyl carbon. Thus, a negative ρ value in $CDCl_3$ is consistent with the positive charge build-up on the *internal* alkynyl carbon, while a positive ρ value in THF suggests of an electrophilic character on the *terminal* alkynyl carbon. Once again, the latter case is consistent with the formation of a Ru-vinylidene species and the addition of the carboxylate group to the electrophilic α-vinylidene carbon in the transition state.

Catalytically Relevant Ruthenium-Carboxylate and –Vinylidene-Carboxylate Complexes

A catalytically relevant ruthenium-carboxylate complex was successfully isolated from the reaction of **1** with a carboxylic acid. For example, the treatment of **1** (72 mg, 0.10 mmol) with *p*-OMe-$C_6H_4CO_2H$ (16 mg, 0.11 mmol) in CH_2Cl_2 (2 mL) at room temperature for 10 h led to the clean formation of the ruthenium-carboxylate complex **6**, which was isolated in 87% yield after recrystallization in CH_2Cl_2/hexanes. The complex **6** exhibited two sets of aryl protons at δ 7.88 (d, J = 8.7 Hz) and 6.89 (d, J = 8.7 Hz) in the ^1H NMR, as well as two carbonyl peaks at δ 208.8 (t, J_{CP} = 13.3 Hz, CO) and 179.0 (s, CO_2) in the $^{13}C\{^1H\}$ NMR. A single phosphine peak at δ 28.7 was also observed by the $^{31}P\{^1H\}$ NMR. The structure of **6** was further established by X-ray crystallography (Figure 4). The molecular structure showed a pseudooctahedral geometry around the ruthenium center with trans phosphine and cis CO and Cl^- ligand arrangements. A slightly larger than 90° bond angle between CO to Cl^- ligands (96.4°) may be due to a κ[2]-bonding mode of the carboxylate ligand.

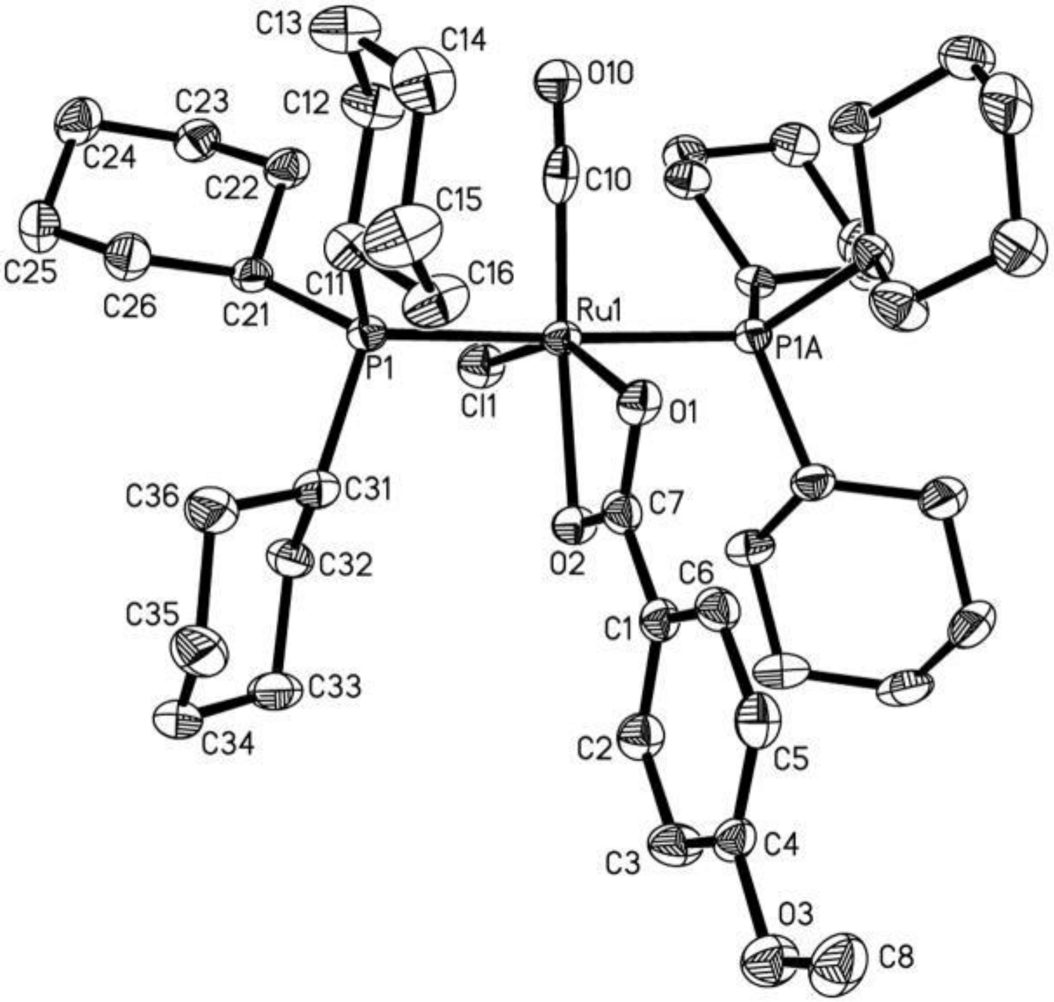


Figure 4. Molecular Structure of **6**.

In an effort to form a catalytically relevant ruthenium-vinylidene complex, the reaction of the ruthenium-carboxylate complex **6** with terminal alkynes was performed in THF. Thus, the treatment of complex **6** (44 mg, 0.050 mmol) with phenylacetylene (1.2 equiv) in THF at 95 °C for 10 h led to the coupling product **7**, which was isolated in 85% yield as a pale yellow-colored solid. The ^{1}H NMR of complex **7** showed a diagnostic vinyl peak at δ 6.24 (br s), and two distinct α-carbonyl peaks at δ 208.8 (t, J_{CP} = 14.4 Hz, Ru-CO) and 190.2 (t, J_{CP} = 12.1 Hz, Ru-*C*(O)CHPh) were also observed by the $^{13}C\{^1H\}$ NMR.

The molecular structure of **7** as determined by X-ray crystallography showed a syn orientation between the carboxylate oxygen atom and the phenyl group that was apparently resulted from

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the coupling between the carboxylate and the vinylidene ligands (Figure 5). The structure clearly implicates the formation of the (*Z*)-enol ester product (*Z*)-**3k** from the protonation by another carboxylic acid. To show the enol ester product formation, the complex **7** was treated with an equivalent of benzoic acid in THF, which produced the carboxylate complex **6** and (*Z*)-**3k** along with another unidentified ruthenium complex upon heating at 90 °C for 2 h. Furthermore, the activity of both complexes **6** and **7** was found to be virtually identical to **1** for the coupling reaction of benzoic acid and phenylacetylene in THF (>90% yield with 2 mol% of **7**).

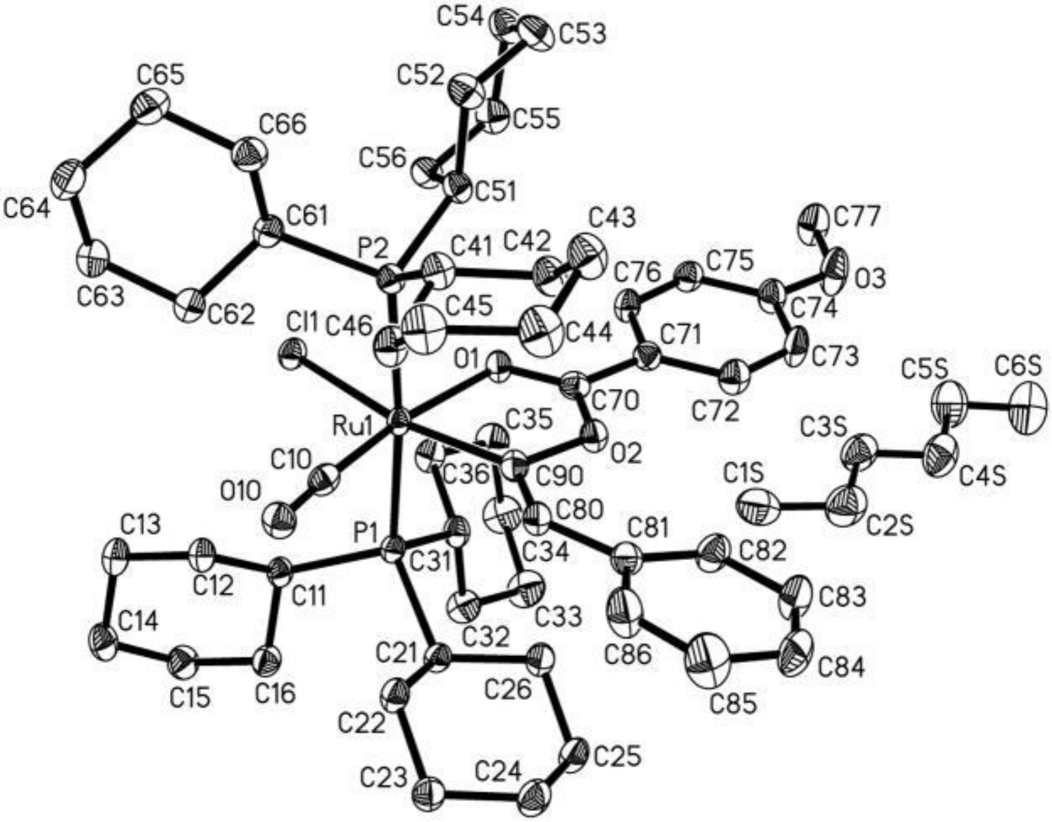
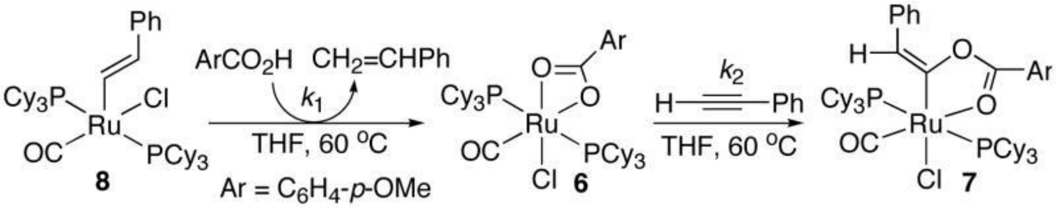


Figure 5. Molecular Structure of **7**.

The successful isolation of the catalytically relevant complexes **6** and **7** enabled us to further examine the kinetics for the formation of these complexes. The treatment of **1** (14 mg, 0.020 mmol) with excess amounts of *p*-OMe-$C_6H_4CO_2H$ (10 equiv) and HC≡CPh (15 equiv) in THF was followed by ^1H and ^{31}P NMR (Scheme 2). As expected, the formation of the previously synthesized ruthenium-vinyl complex **8** was observed after 15 min at room temperature.[23] Upon warming to 40 °C, the vinyl complex **8** was slowly converted to the carboxylate complex **6** within 10 min along with the formation of styrene. At 60 °C, the signals due to the vinylidene-carboxylate complex **7** gradually appeared at the expense of the carboxylate complex **6**. Eventually, the formation of the coupling product (Z)-**3k** along with $Cy_3PH^+PhCO_2^-$ was observed after heating at 90 °C for 2 h.



Scheme 2

The kinetics of the conversion of the vinyl complex **8** to the vinylidene-carboxylate complex **7** was followed by ^{31}P NMR (Figure 6). In a J-Young NMR tube, **1** (14 mg, 0.020 mmol), 4-methoxybenzoic acid (30 mg, 0.20 mmol) and phenylacetylene (31 mg, 0.30 mmol) were dissolved in THF (0.5 mL). The formation of the vinyl complex **8** was completed within 10 min at room temperature. The appearance of **6** and **7** was monitored by ^{31}P NMR at 60 °C in 5 min intervals. The experimental data was successfully fitted to the kinetic equation for two consecutive reaction kinetics by using non-linear regression techniques for the conversion of **8** to **7** (Sigmaplot Version 10).[24] The rate constants $k_1 = 0.039\ \text{min}^{-1}$ and $k_2 = 0.013\ \text{min}^{-1}$ were obtained from this analysis. A relatively smaller value of k_2 compared to k_1 is consistent with the rate-limiting C-O bond formation step.

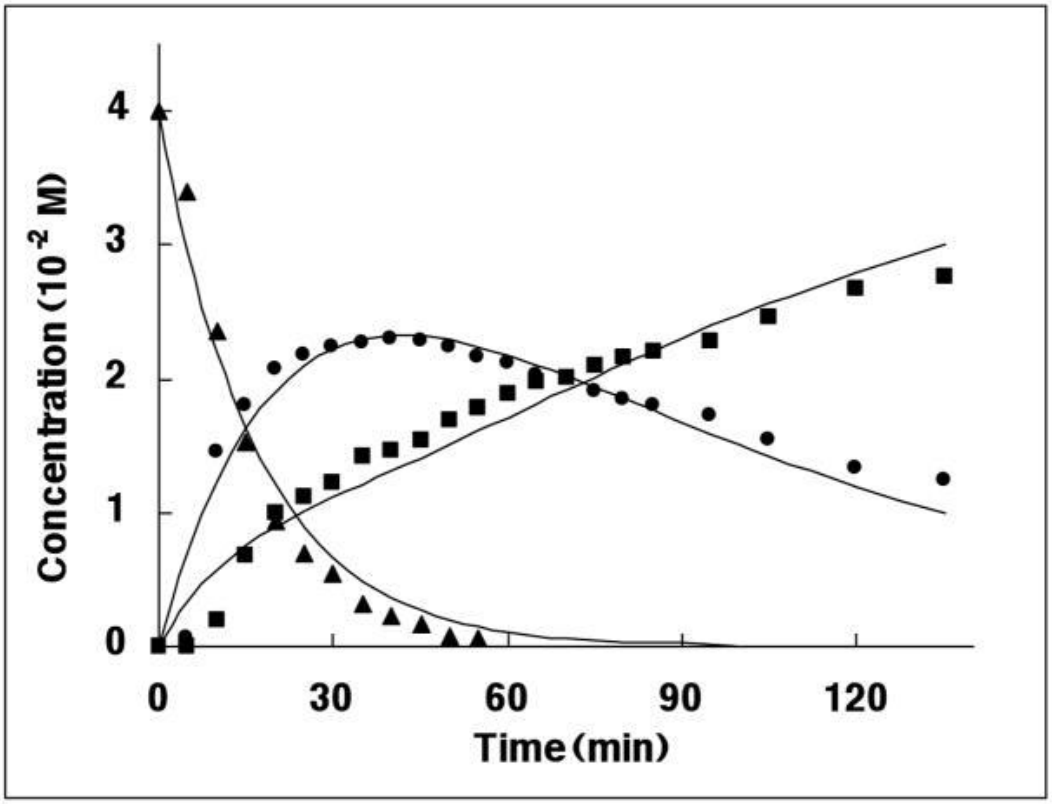


Figure 6. Kinetic Profile of the Conversion of **8** to **7**. Notations: **8** (▲), 6 (●), **7** (■).

Proposed Mechanism

We propose a mechanism of the coupling reaction involving a coordinatively unsaturated ruthenium-carboxylate complex **9** as one of the key intermediate species (Scheme 3). The phosphine inhibition study suggests that the catalytically active 16 e- complex **9** is formed from the Ru-carboxylate complex **6** by a reversible phosphine dissociation. For the coupling reaction in a non-coordinating solvent such as CH_2Cl_2, the direct migratory insertion of the carboxylate oxygen to the internal carbon of the alkyne substrate would be preferred over to the terminal one to give the *gem*-enol ester product **2**. The dative coordination of carboxylic oxygen atom would also promote the insertion by stabilizing intermediate species. On the other hand, the formation of (*Z*)-enol ester product (*Z*)-**3** is rationalized by invoking the formation of Ru-vinylidene species **10**. It has been well-established that the acetylene-to-vinylidene rearrangement is relatively facile for aryl-substituted alkynes. [10,21] The ability to promote the acetylene-to-vinylidene rearrangement for the ruthenium-catalyst

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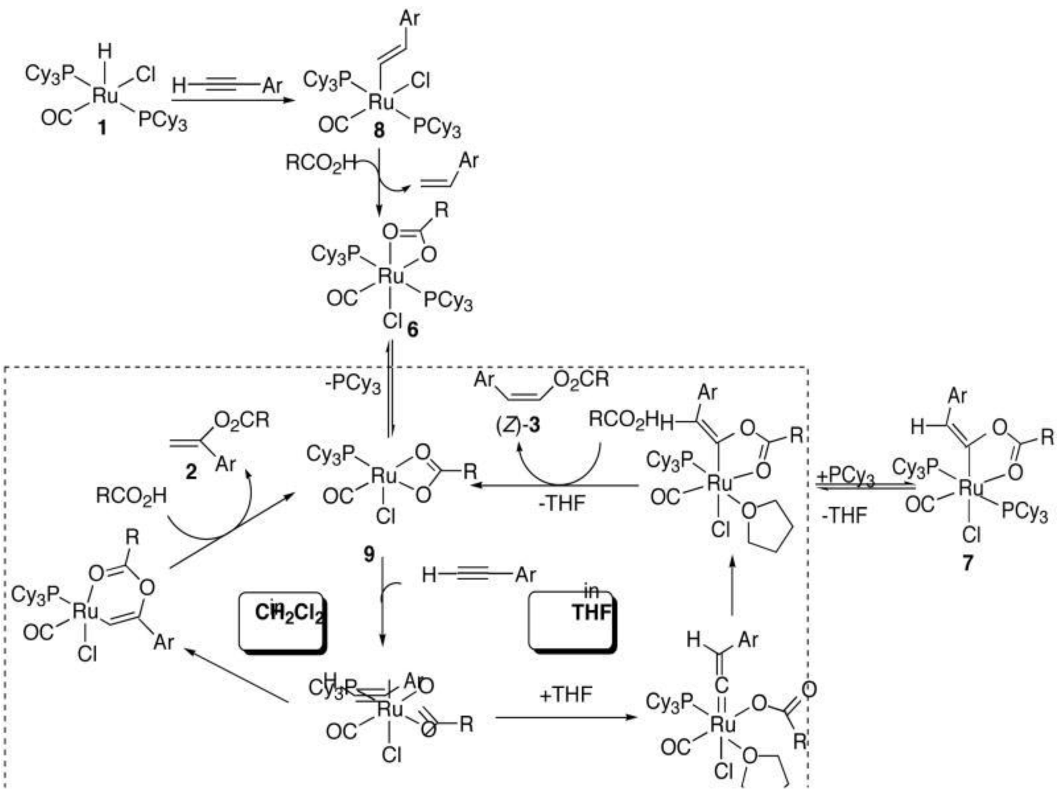
should be an important factor for the stereoselective formation of (*Z*)-enol ester products, and the coordinating solvent THF would facilitate such rearrangement by stabilizing a corrdinatively unsaturated Ru-vinylidene species.



Scheme 3. Proposed Mechanism of the Coupling Reaction of Carboxylic Acids and Terminal Alkynes.

The Hammett study suggested that the C-O bond formation of the catalytic coupling reaction is strongly influenced by the electronic nature of the substrates. For the coupling reaction in CH_2Cl_2, this implies a direct migratory insertion of the coordinated terminal alkyne to the Ru-carboxylic oxygen bond, where both steric and electronic factors dictate the Markovnikov-selective formation of the *gem*-enol ester product **2**. The dative coordination of the carbonyl oxygen to the Ru center would also facilitate this transformation by avoiding the formation of a high-energy 14-electron species.

The successful isolation of **6** and **7** and their kinetic reaction profile provided new mechanistic insights for the formation of (*Z*)-enol ester product (*Z*)-**3**. The reversible dissociation of PCy_3 from both complexes **6** and **7** should form the catalytically active species for the coupling reaction, and in this regard, the formation of Cy_3PH^+ from the protonation of free PCy_3 by the carboxylic acid substrate would prohibit the re-coordination of the phosphine ligand to the Ru center. The syn geometry of the vinylidene-carboxylate ligand of **7** clearly indicates that the formation of (*Z*)-enol ester product (*Z*)-**3** is electronically controlled during the addition of carboxylate group to the α-vinylidene ligand of the ruthenium-vinylidene species **10**. Such cis addition of the carboxylate group could also be facilitated by the dative coordination of the carboxylate oxygen atom. A complementary computational study on the catalytic coupling reaction would be prudent in identifying these catalytically active intermediate species.

Concluding Remarks

The ruthenium-hydride complex **1** was found to be a highly effective catalyst for the alkyne-to-carboxylic acid coupling reaction to give synthetically valuable enol esters. Regio- and stereoselectivity of the catalyst **1** was successfully controlled by using CH_2Cl_2 and THF. From a synthetic point of view, the ruthenium catalyst **1** exhibited a number of salient features including: its ability to control the activity and selectivity on the enol ester product formation with a relatively low catalyst loading, and a broad substrate scope under relatively moderate reaction conditions. The kinetic and mechanistic investigations as well as the successful isolation of Ru-carboxylate and –vinylidene-carboxylate complexes **6** and **7** provided a detailed mechanistic picture for the coupling reaction. The mechanistic knowledge gained from this study should give invaluable insights in designing the next generation of metal catalysts for the alkyne-to-carboxylic acid coupling reaction.

Experimental Section

General Information

All operations were carried out in a nitrogen-filled glove box or by using standard high vacuum and Schlenk techniques unless otherwise noted. Tetrahydrofuran, benzene, hexanes and Et_2O were distilled from purple solutions of sodium and benzophenone immediately prior to use. The NMR solvents were dried from activated molecular sieves (4 Å). All carboxylic acids and alkyne substrates were received from commercial sources and used without further purification. $RuCl_3 \cdot 3H_2O$ and $Ru_3(CO)_{12}$ were obtained from commercial sources, and the complex **1** was prepared by following a reported procedure.[23] The ^1H, ^2H, ^{13}C and ^{31}P NMR spectra were recorded on a Varian Mercury 300 or 400 MHz FT-NMR spectrometer. Mass spectra were recorded from a Agilent 6850 GC/MS spectrometer. The conversion of organic products was measured from a Hewlett-Packard HP 6890 GC spectrometer. Elemental analyses were performed at the Midwest Microlab, Indianapolis, IN.

General Procedure of the Catalytic Reaction

In a glove box, a carboxylic acid (1.0 mmol), a terminal alkyne (2.0 mmol) and the ruthenium catalyst **1** (14 mg, 2 mol %) were dissolved in 3 mL of CH_2Cl_2 (or THF) in a 25 mL Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar. The reaction tube was brought out of the box, and was stirred in an oil bath at 90–95 °C for 10–12 h. The tube was opened to air at room temperature, and the crude product mixture was analyzed by GC. Analytically pure organic product was isolated by a column chromatography on silica gel (hexanes/EtOAc). While we have not encountered any problems, the reaction in CH_2Cl_2 must be carried out with extra caution because of its relatively low boiling point. A thick-walled Schelnk tube with enough volume reservoir is strongly recommended.

Phosphine Inhibition Study

In a glove box, benzoic acid (24 mg, 0.20 mmol), phenylacetylene (40mg, 0.40 mmol), **1** (3 mg, 2 mol %) and C_6Me_6 (5 mg, internal standard) were dissolved in $CDCl_3$ (0.5 mL) in a J-Young NMR tube with a Teflon screw cap. A predissolved PCy_3 in $CDCl_3$ solution (5–15 μL, 10–30 m*M*) was added to the tube via syringe. The tube was brought out of the glove box and was heated in an oil bath at 95 °C. The reaction was monitored by ^1H NMR in 30 min intervals. The rate was measured by the ^1H integration of the product peak at δ 5.61 ($=CH_2$), and was normalized against the internal standard peak. The

k_{obs} was estimated from the first order plot of *ln*[product] vs reaction time.

Isotope Labeling Study

In a glove box, benzoic acid (122 mg, 1.0 mmol) and DC≡CPh (206 mg, 2.0 mmol) were added via syringe to a 25 mL Schlenk tube equipped with a magnetic stirring bar and Teflon stopcock. The pre-dissolved catalyst **1** (14 mg, 2 mol %) in CH_2Cl_2 or THF (3 mL) was added to the reaction tube. The reaction tube was brought out of the box, and was stirred in an oil bath at 95 °C for 10 h. The solvent was removed from a rotary evaporator, and the organic product was isolated by a column chromatography on silica gel (hexanes/CH_2Cl_2 = 3:2). The deuterium content of the product **2c** and **3c** was measured from both ^{1}H NMR ($CDCl_3$ with 10 mg cyclohexane as the external standard) and ^{2}H NMR (CH_2Cl_2 with 50 μL $CDCl_3$).

Hammett Study: Reaction in $CDCl_3$

In a glove box, a *para*-substituted acid *p*-X-$C_6H_4CO_2H$ (X = OMe, CH_3, H, CF_3, CN) (0.20 mmol), phenylacetylene (40 mg, 0.40 mmol), **1** (3 mg, 2 mol %) and C_6Me_6 (5 mg, internal standard) were dissolved in $CDCl_3$ (0.5 mL) solution in a J-Young NMR tube with a Teflon screw cap. The tube was brought out of the glove box and was heated in an oil bath set at 95 °C. The reaction was monitored by ^{1}H NMR in 10 min intervals. The k_{obs} was estimated from a first–order plot of *ln*[product] vs reaction time by measuring the ^{1}H integration of the product peak (=CH_2, δ 5.61 ppm), which was normalized against the internal standard peak. **Reaction in THF:** In a 25 mL Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar, a *para*-substituted acid *p*-X-$C_6H_4CO_2H$ (X = OMe, CH_3, H, CF_3, CN) (0.20 mmol), phenylacetylene (40 mg, 0.40 mmol), **1** (3 mg, 2 mol %) and C_6Me_6 (5 mg, internal standard) were dissolved in THF (3 mL) in a glove box. The tube was brought out of the glove box, and was heated in an oil bath at 95 °C. The reaction was monitored by GC in 10 min intervals. The k_{obs} was estimated from a first–order plot of *ln*[product] vs reaction time by measuring the amount of the products against the internal standard.

Kinetic Profile Experiment

In a glove box, **1** (14 mg, 0.02 mmol), 4-methoxybenzoic acid (30 mg, 0.20 mmol) and HC≡CPh (31 mg, 0.30 mmol) were dissolved in THF (0.5 mL) in a J-Young NMR tube with a Teflon screw cap. The tube was brought out of the glove box, and was placed in NMR probe which was preset at 60 °C. The appearance and disappearance of the phosphine signals for **8** (δ 24.4), **6** (δ 25.9) and **7** (δ 23.4) were monitored by ^{31}P NMR at 60 °C in 5 min intervals. The rate of the product formation was determined by measuring the integration of the product peaks against the disappearance of the complex **8**. By using a non-linear regression technique (Sigmaplot Version 10), the experimental data was globally fitted to the kinetic equation as shown in Figure 6. The rate constants k_1= 0.039 min^{-1} and k_2 = 0.013 min^{-1} were obtained from this analysis.

Synthesis of $(PCy_3)_2(CO)(Cl)Ru(\kappa^2\text{-}O_2CC_6H_4\text{-}p\text{-}OMe)$ (6)

In a glove box, 4-methoxybenzoic acid (13 mg, 0.10 mmol), phenylacetylene (10 mg, 0.10 mmol), and complex **1** (73 mg, 0.10 mmol) were dissolved in CH_2Cl_2 (3 mL) in a 25 mL Schlenk tube equipped with a Teflon screw cap stopcock and a magnetic stirring bar. The tube was brought out of the box, and was stirred at room temperature for 10 h. The solvent was evaporated and the residue was washed with hexanes (3 mL × 3 times) to obtain **6** in 87% yield. Single crystals suitable for X-ray crystallographic study were obtained from hexanes/CH_2Cl_2.

For **6**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.7 Hz, Ph), 6.89 (d, *J* = 8.7 Hz, Ph), 3.86 (s, OCH_3), 2.30-1.01 (m, PCy_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 208.8 (t, J_{CP} = 13.3 Hz, CO), 179.0 (s, CO_2), 162.9, 130.3, 125.1 and 113.6 (C_{Ar}), 55.5 (OCH_3), 34.1, 30.2, 29.7, 28.3 and 26.8 (PCy_3); $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$) δ 28.7 (s, PCy_3); IR (KBr) ν_{CO} = 1913 cm^{-1}.

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Synthesis of $(PCy_3)_2(CO)(Cl)RuC(=CHPh)O_2CC_6H_4$-p-OMe (7)

In a glove box, the Ru-carboxylate complex **6** (44 mg, 50 μmol) and phenylacetylene (6 mg, 60 μmol) were dissolved in THF (3 mL) in a 25 mL Schlenk tube equipped with a Teflon screw cap stopcock and a magnetic stirring bar. The tube was brought out of the glove box and was heated in an oil bath at 95 °C for 10 h. The solvent was removed under high vacuum, and the residue was washed with hexanes (5 mL × 3 times) to obtain analytically pure **7** in 85% yield. Single crystals suitable for X-ray crystallographic study were obtained from hexanes/CH_2Cl_2.

For **7**: ^{1}H NMR (400 MHz, C_6D_6) δ 8.44 (d, J = 8.7 Hz, 2H, Ph), 7.76 (d, J = 7.7 Hz, 2H, Ph), 7.36-6.63 (m, Ar), 6.24 (s, =CHPh), 2.98 (s, OCH_3), 2.71-0.8 (m, PCy_3); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) 209.8 (t, J_{PC} = 14.4 Hz, CO), 190.2 (t, J_{PC} = 12.2 Hz, Ru-*C*=CH), 173.8 (CO_2), 167.9, 165.4, 138.4, 133.8, 129.1, 125.0, 122.5 and 120.0 (C_{Ar}), 115.1 (=CH), 55.4 (OCH_3), 35.2, 31.1, 30.6, 29.8, 28.8 and 27.3 (PCy_3); ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$) δ 27.0 (s, PCy_3); IR (KBr) ν_{CO} = 1922 cm^{-1}.

Acknowledgments

Financial support from the National Institute of Health, General Medical Sciences (R15 GM55987) is gratefully acknowledged. We also thank Dr. Sergey Lindeman (Marquette University) for X-ray crystallographic determination of the ruthenium complexes.

Footnotes

Supporting Information Available: Spectroscopic data of organic products and X-ray crystallographic data of **6** and **7** (77 pages, print/PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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24. See Supporting Information for the derivation of kinetic equation.

Supplementary Material

1_si_001

Supporting Information

Scope and Mechanistic Investigations on the Solvent-Controlled Regio- and Stereoselective Formation of Enol Esters from the Ruthenium-Catalyzed Coupling Reaction of Terminal Alkynes and Carboxylic Acids

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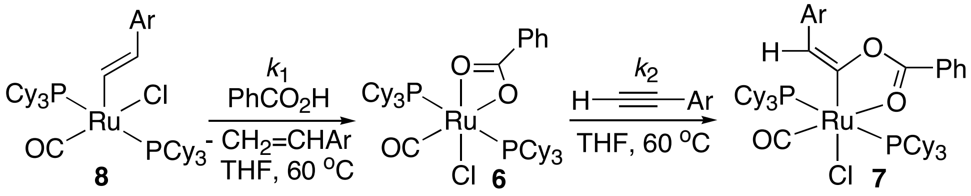
Derivation of the Kinetic Equation of the Conversion of 8 to 7



The derivation for two consecutive first–order reaction was followed the method described in: Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*, 3rd Ed.; Wiley: New York, 1981, pp. 290-296.

$d[\mathbf{8}]/dt = -k_1 t$

$d[\mathbf{6}]/dt = k_1[\mathbf{4}] - k_2[\mathbf{6}]$

$d[7]/dt = k_2[\mathbf{6}]$

$[\mathbf{8}] = [\mathbf{8}]_0 e^{-k1t}$

$d[\mathbf{6}]/dt = k_1[\mathbf{8}]_0 e^{-k1t} - k_2[\mathbf{6}]$

$[\mathbf{6}] = [\mathbf{8}]_0 k_1(e^{-k1t} - e^{-k2t})/(k_2 - k_1)$

$d[\mathbf{8}]/dt + d[\mathbf{6}]/dt + d[7]/dt = 0$

Since

$[\mathbf{8}] + [\mathbf{6}] + [7] = [\mathbf{8}]_0$

$[\mathbf{6}]_0 = [7]_0 = 0$

$[7] = [\mathbf{4}]_0 - [\mathbf{4}] - [\mathbf{8}]$

$\quad = [\mathbf{8}]_0[1 + (k_2 e^{-k1t} - k_1 e^{-k2t})/(k_1 - k_2)$

$d[7]/dt = [\mathbf{8}]_0 k_1 k_2[(e^{-k1t} - e^{-k2t})/(k_1 - k_2)$

The experimental data was globally fitted to the kinetic equation by using non-linear regression techniques (Sigmaplot V. 10). The rate constants k_1= 0.039 min^{-1} and k_2 = 0.013 min^{-1} were obtained and from this analysis.

$$
\begin{aligned}
d[\mathbf{7}]/dt &= [\mathbf{8}]_0{*}0.039{*}0.013{*}(e^{-0.039t} - e^{-0.013t})/(0.039 - 0.013) \\
&= [\mathbf{8}]_0{*}0.0195{*}(e^{-0.039t} - e^{-0.013t})
\end{aligned}
$$

Characterization Data of Organic Products

For **2a:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15-6.70 (m, 9H, Ph), 5.37 (d, *J* = 2.1 Hz, $=CH_2$), 4.98 (d, *J* = 2.1 Hz, $=CH_2$), 3.69 (s, 3H, OCH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 165.1 ($PhCO_2$), 160.5 (CH_2=*C*), 153.2, 133.8, 130.4, 129.8, 128.8, 127.2, 126.6 and 114.2 (C_{Ar}), 100.7 (*C*H_2=C), 55.5 (OCH_3); GC-MS *m/z* = 254 (M^+).

For **2b:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25-7.10 (m, 9H, Ph), 5.57 (d, *J* = 2.1 Hz, $=CH_2$), 5.14 (d, *J* = 2.1 Hz, $=CH_2$), 2.37 (s, CH_3); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.9 (Ph*C*O_2), 153.3 (CH_2=*C*), 139.0, 133.6, 131.6, 130.1, 129.6, 129.3, 128.5 and 124.8 (C_{Ar}), 100.4 (*C*H_2=C), 21.3 (CH_3); GC-MS *m/z* = 238 (M^+).

For **2c:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05-7.10 (m, 10H, Ph), 5.57 (d, *J* = 1.9 Hz, $=CH_2$), 5.09 (d, *J* = 1.9 Hz, $=CH_2$); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 164.9 (Ph*C*O_2), 153.3 (CH_2=*C*), 134.4, 133.8, 130.2, 129.5, 129.1, 128.8, 128.7 and 125.0 (C_{Ar}), 102.5 (*C*H_2=C); GC-MS *m/z* = 224 (M^+).

For **2d:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25-7.38 (m, 9H, Ph), 5.60 (d, *J* = 2.4 Hz, $=CH_2$), 5.21 (d, *J* = 2.4 Hz, $=CH_2$); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 165.1 (Ph*C*O_2), 152.5 (CH_2=*C*), 134.0, 133.6, 132.0, 130.4, 129.5, 126.8 and 123.4 (C_{Ar}), 103.2 (*C*H_2=C); GC-MS *m/z* = 303 (M^+).

For **2e:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25-7.38 (m, 9H, Ph), 5.69 (d, *J* = 2.4 Hz, $=CH_2$), 5.30 (d, *J* = 2.4 Hz, $=CH_2$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.1 (Ph*C*O_2), 152.5 (CH_2=*C*), 134.0, 133.6, 132.0, 130.4, 129.5, 126.8 and 123.4 (C_{Ar}), 103.2 (*C*H_2=C); GC-MS *m/z* = 303 (M^+).

For **2f:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25-7.00 (m, 9H, Ph), 5.53 (d, *J* = 2.4 Hz, $=CH_2$), 5.16 (d, *J* = 2.4 Hz, $=CH_2$); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 165.1 (Ph*C*O_2), 161.7 (CH_2=*C*), 152.5, 133.9, 130.8, 130.3, 129.5, 128.9, 127.1 and 115.7 (C_{Ar}), 102.4 (*C*H_2=C); GC-MS *m/z* = 242 (M^+); Anal. Calcd for $C_{15}H_{11}FO_2$: C, 74.37; H, 4.58. Found: C, 73.27; H, 4.50.

For **2g:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15-7.38 (m, 5H, Ph), 4.87 (s, $=CH_2$), 4.83 (s, $=CH_2$), 2.34 (t, 2H, $=CH_2CH_2$), 1.53 (m, 2H, $=CH_2CH_2CH_2CH_2$), 1.39 (m, 2H, $=CH_2CH_2CH_2CH_2CH_3$), 0.92 (t, CH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 164.8 (Ph*C*O_2), 156.9 (CH_2=*C*), 133.3, 130.0, 129.6 and 128.5 (C_{Ar}), 101.3 (*C*H_2=C), 33.2 ($=CH_2CH_2$), 28.7 ($=CH_2CH_2CH_2CH_2CH_3$), 22.2 (CH_2CH_3), 13.9 (CH_3); GC-MS *m/z* = 204 (M^+).

For **2h:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15-7.30 (m, 10H, Ph), 5.08 (d, *J* = 2.4 Hz, $=CH_2$), 4.90 (d, *J* = 2.4 Hz, $=CH_2$), 3.75 (s, 2H, $=CH_2CH_2Ph$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ

164.8 (Ph*C*O$_2$), 155.8 (CH$_2$=*C*), 137.0, 133.5, 130.0, 129.8, 129.6, 128.6 and 126.9 (C$_{Ar}$), 103.6 (*C*H$_2$=C), 40.1 (*C*H$_2$Ph); GC-MS *m/z* = 238 (M$^+$).

For **2i:** ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.20-7.38 (m, 5H, Ph), 5.22 (d, *J* = 2.4 Hz, =CH$_2$), 5.03 (d, *J* = 2.4 Hz, =CH$_2$), 2.0 (s, CH$_3$); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$) δ 164.6 (Ph*C*O$_2$), 153.7 (CH$_2$=*C*), 136.6, 133.5, 130.0, 129.5 and 128.6 (C$_{Ar}$), 113.9 (C*C*H$_2$CH$_3$), 103.6 (=CH$_2$*C*H$_2$), 19.4 (CH$_3$); GC-MS *m/z* = 188 (M$^+$).

For **2j:** ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.35-7.10 (m, 11H, Ar), 5.70 (d, *J* = 2.4 Hz, =CH$_2$), 5.23 (d, *J* = 2.4 Hz, =CH$_2$), 3.90 (OCH$_3$); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$) δ 165.2 (Ph*C*O$_2$), 158.4 (CH$_2$=*C*), 153.5, 135.0, 133.8, 130.3, 129.7, 129.6, 128.8, 127.4, 124.1, 123.4, 119.4 and 105.9 (C$_{Ar}$), 102.1 (*C*H$_2$=C), 55.5 (O*C*H$_3$); GC-MS *m/z* = 304 (M$^+$); Anal. Calcd for $C_{16}H_{14}O_2$: C, 78.93; H, 5.30. Found: C, 78.76; H, 5.37.

For **2k:** ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.25-6.95 (m, 9H, Ph), 5.62 (d, *J* = 2.4 Hz, =CH$_2$), 5.19 (d, *J* = 2.4 Hz, =CH$_2$), 3.87 (s, 3H, OCH$_3$); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$) δ 164.6 (Ph*C*O$_2$), 164.0 (CH$_2$=*C*), 153.3, 134.5 132.3, 129.0, 128.6, 125.0, 121.8 and 114.2 (C$_{Ar}$), 102.3 (*C*H$_2$=C), 55.5 (O*C*H$_3$); GC-MS *m/z* = 254 (M$^+$).

For **2l:** ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.20-7.32 (m, 9H, Ph), 5.66 (d, *J* = 2.1 Hz, =CH$_2$), 5.23 (d, *J* = 2.1 Hz, =CH$_2$), 2.48 (s, CH$_3$); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ 164.9 (Ph*C*O$_2$), 153.3 (CH$_2$=*C*), 144.5, 134.4, 132.2, 130.1, 129.6, 129.0, 128.5 and 126.8 (C$_{Ar}$), 102.4 (*C*H$_2$=C), 21.8 (CH$_3$); GC-MS *m/z* = 238 (M$^+$)

For **2m:** ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.00-7.20 (m, 9H, Ph), 5.50 (d, *J* = 2.4 Hz, =CH$_2$), 5.07 (d, *J* = 2.4 Hz, =CH$_2$); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$) δ 164.3 (Ph*C*O$_2$), 153.2 (CH$_2$=*C*), 134.2, 132.2, 131.8, 129.3, 129.0, 128.8, 128.5 and 125.0 (C$_{Ar}$), 102.7 (*C*H$_2$=C); GC-MS *m/z* = 303 (M$^+$).

For **2n:** ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.30-7.00 (m, 9H, Ph), 5.52 (d, *J* = 2.4 Hz, =CH$_2$), 5.10 (d, *J* = 2.4 Hz, =CH$_2$); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ 163.3 (Ph*C*O$_2$), 153.2 (CH$_2$=*C*), 133.9, 133.3, 132.7, 130.7, 129.3, 128.8, 128.5, 125.0, 118.0 and 117.1 (C$_{Ar}$), 102.7 (*C*H$_2$=C); GC-MS *m/z* = 249 (M$^+$); Anal. Calcd for $C_{16}H_{11}NO_2$: C, 77.10; H, 4.45. Found: C, 77.30; H, 4.47.

For **2o:** ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.38-7.32 (m, 9H, Ph), 5.64 (d, *J* = 2.4 Hz, =CH$_2$), 5.20 (d, *J* = 2.4 Hz, =CH$_2$); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$) δ 163.8 (Ph*C*O$_2$), 153.2 (CH$_2$=*C*), 135.4, 135.0, 134.1, 132.8, 130.7, 129.5, 128.8, 125.9 and 122.4 (C$_{Ar}$), 102.8 (*C*H$_2$=C); GC-MS *m/z* = 292 (M$^+$); Calcd for $C_{16}H_{11}F_3O_2$: C, 65.76; H, 3.80. Found: C, 65.51; H, 3.82.

For **2p:** ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.92 (s, PhC*H*), 7.40-6.90 (m, 15H, Ph), 5.38 (d, *J* = 2.4 Hz, =CH$_2$), 5.01 (d, *J* = 2.4 Hz, =CH$_2$); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ 166.1 (Ph*C*O$_2$), 153.4 (CH$_2$=*C*), 142.1, 135.7, 134.5, 134.4, 132.0, 131.0, 129.9, 129.6, 129.0, 128.9, 128.6, 128.4 and 125.0 (C$_{Ar}$), 102.8 (*C*H$_2$=C); GC-MS *m/z* = 326 (M$^+$); Calcd for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56. Found: C, 84.40; H, 5.55.

For **2q:** ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.97 (s, PhC*H*), 7.47-7.08 (m, 15H, Ph), 4.86 (d, *J* = 2.4 Hz, =CH$_2$), 4.79 (d, *J* = 2.4 Hz, =CH$_2$), 2.43 (t, 2H, =CH$_2$C*H*$_2$), 1.55 (m, 4H, C*H*$_2$C*H*$_2$CH$_3$), 1.03 (t, CH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 166.1 (Ph*C*O_2), 157.0 (CH_2=*C*), 141.3, 135.7, 134.5, 132.4, 130.8, 129.9, 129.3, 1287 and 128.4 (C_{Ar}), 101.0 (*C*H_2=C), 33.1 (=CCH_2*C*H_2), 28.7 (*C*$H_2CH_2CH_3$), 14.0 (CH_3), 2.1 (*C*H_2CH_3); GC-MS *m/z* = 306 (M^+).

For **2r:** ^1H NMR (400 MHz, $CDCl_3$) δ 7.52-7.30 (m, 5H, Ph), 5.53 (d, *J* = 2.4 Hz, =CH_2), 5.01 (d, *J* = 2.4 Hz, =CH_2), 2.56 (m, $CHCO_2$), 2.09-1.83 (m, 4H, C*H_2*CHC*H_2*CO_2), 1.7-1.2 (m, 6H, CH_2); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 174.2 (*C*O_2), 153.1 (CH_2=*C*), 134.7, 129.0, 128.6 and 125.0 (C_{Ar}), 102.0 (*C*H_2=C), 43.4, 29.1, 25.8 and 25.5 (CH_2); GC-MS *m/z* = 230 (M^+); Calcd for $C_{15}H_{18}O_2$: C, 78.22; H, 7.87. Found: C, 78.09; H, 7.66.

For **2s:** ^1H NMR (400 MHz, $CDCl_3$) δ 7.52-7.30 (m, 5H, Ph), 5.48 (d, *J* = 2.4 Hz, =CH_2), 5.01 (d, *J* = 2.4 Hz, =CH_2), 2.56 (t, CH_2CO_2), 1.74 (m, 2H, C*H_2*CH_2CO_2), 1.44-1.20 (m, 24H, CH_2), 0.89 (t, CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 172.2 (*C*O_2), 153.1 (CH_2=*C*), 134.7, 129.0, 128.6 and 125.0 (C_{Ar}), 102.4 (*C*H_2=C), 34.5, 31.2, 30.0, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 25.1 and 22.9 (CH_2) and 14.3 (CH_3); GC-MS *m/z* = 230 (M^+); Calcd for $C_{24}H_{38}O_2$: C, 80.40; H, 10.68. Found: C, 80.55; H, 10.46.

For (*Z*)-**3a:** ^1H NMR (300 MHz, $CDCl_3$) δ 8.10-6.63 (m, 9H, Ph), 7.38 (d, *J* = 7.4 Hz, =CH), 5.71 (d, *J* = 7.4 Hz, =CH), 3.73 (s, OCH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 163.8 (Ph*C*O_2), 159.1, 133.8, 133.0, 130.8, 130.3, 129.3, 129.0, 127.1, 114.2 and 112.5 (C_{Ar}), 55.5 (OCH_3); GC-MS *m/z* = 254 (M^+).

For (*Z*)-**3b**: ^1H NMR (400 MHz, $CDCl_3$) δ 8.05-7.05 (m, 9H, Ph), 7.98 (d, *J* = 12.8 Hz, =CH), 6.47 (d, *J* = 12.8 Hz, =CH), 2.25 (s, CH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 163.7 (Ph*C*O_2), 137.4, 135.9, 133.7, 133.6, 131.1, 130.0, 129.5, 129.0, 128.6 and 115.8 (C_{Ar} and =CH), 21.3 (CH_3); GC-MS *m/z* = 238 (M^+); Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.74; H, 5.99.

For (*Z*)-**3c**: ^1H NMR (300 MHz, $CDCl_3$) δ 8.05-7.10 (m, 10H, Ph), 7.40 (d, *J* = 7.4 Hz, C*H*=CHPh), 5.76 (d, *J* = 7.4 Hz, CH=C*H*Ph); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 163.5 ($PhCO_2$), 134.2, 134.1, 133.8, 130.2, 129.2, 128.9 128.8, 128.5, 127.4 and 112.7 (C_{Ar} and =CH); GC-MS *m/z* = 224 (M^+).

For (*Z*)-**3d:** ^1H NMR (300 MHz, $CDCl_3$) δ 8.15-7.24 (m, 9H, Ph), 7.50 (d, *J* = 7.4 Hz, 1H, =CH), 5.80 (d, *J* = 7.4 Hz, =CH); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 163.8 (Ph*C*O_2), 159.1, 133.8, 133.0, 130.8, 130.3, 129.3, 129.0, 127.1 and 114.2 (C_{Ar} and =CH), 112.5 (=C*C*H_2), 55.5 (CH_3); GC-MS *m/z* = 303 (M^+); Calcd for $C_{15}H_{11}BrO_2$: C, 59.42; H, 3.66. Found: C, 59.06; H, 3.64.

For (*Z*)-**3e:** ^1H NMR (400 MHz, $CDCl_3$) δ 8.20-7.50 (m, 9H, Ph), 7.53 (d, *J* = 7.4 Hz, =CH), 5.89 (d, *J* = 7.4 Hz, =CH); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 163.8 (Ph*C*O_2), 159.1, 133.8, 133.0, 130.8, 130.3, 129.3, 129.0, 127.1 and 114.2 (C_{Ar} and =CH), 112.5 (=C*C*H_2) and 55.5 (CH_3); GC-MS *m/z* = 292 (M^+).

For (*Z*)-**3f:** ^1H NMR (400 MHz, $CDCl_3$) δ 8.24-7.00 (m, 9H, Ph), 7.50 (d, *J* = 7.4 Hz, =CH), 5.83 (d, *J* = 7.4 Hz, =CH); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.6 (Ph*C*O_2), 163.2, 160.8, 134.1, 134.0, 131.1, 130.3, 129.0 and 128.8 (C_{Ar}), 115.7 and 111.7 (=CH); GC-MS *m/z* = 242 (M^+); Calcd for $C_{15}H_{11}FO_2$: C, 74.37; H, 4.58. Found: C, 73.27; H, 4.50.

For (*Z*)-**3j:** ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.30-7.14 (m, 11H, Ar), 7.53 (d, *J* = 7.4 Hz, =CH), 6.0 (d, *J* = 7.4 Hz, =CH), 3.95 (OCH$_3$); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$) δ 163.6 (Ph*C*O$_2$), 158.2, 134.1, 133.8, 130.3, 129.8, 129.7, 129.2, 128.9, 128.5, 127.8, 127.1, 119.3, 113.0 and 105.9 (C$_{Ar}$ and =CH), 55.5 (OCH$_3$); GC-MS *m/z* = 304 (M$^+$); Anal. Calcd for $C_{16}H_{14}O_2$: C, 78.93; H, 5.30. Found: C, 78.76; H, 5.37.

For (*Z*)-**3k:** ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.20-6.96 (m, 9H, Ph), 7.56 (d, *J* = 7.4 Hz, =CH), 5.85 (d, *J* = 7.4 Hz, =CH), 3.89 (s, OCH$_3$); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$) δ 164.2 (Ph*C*O$_2$), 163.3, 134.5, 134.4, 132.4, 129.3, 128.6, 127.4 and 121.2 (C$_{Ar}$), 114.2 and 112.3 (=CH), 55.5 (OCH$_3$); GC-MS *m/z* = 254 (M$^+$).

For (*Z*)-**3l**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.12-7.24 (m, 9H, Ph), 7.58 (d, *J* = 12.8 Hz, =CH), 5.88 (d, *J* = 12.8 Hz, =CH), 2.47 (s, CH$_3$); ^{13}C{^{1}H} NMR (400 MHz, CDCl$_3$) δ 163.4 (Ph*C*O$_2$), 144.8, 134.4, 134.3, 130.2, 129.5, 129.2, 128.6, 127.3 and 126.3 (C$_{Ar}$ and =CH), 112.4 (Ph*C*H=), 21.8 (CH$_3$); GC-MS *m/z* = 238 (M$^+$); Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.74; H, 5.99.

For (*Z*)-**3n**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.30-7.24 (m, 9H, Ph), 7.58 (d, *J* = 12.8 Hz, =CH), 5.94 (d, *J* = 12.8 Hz, =CH); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ 162.0 (Ph*C*O$_2$), 133.9, 133.8, 132.9, 132.7, 130.7, 129.3, 128.8, 127.9, 117.9 and 117.2 (C$_{Ar}$ and =CH), 113.8 (Ph*C*H=); GC-MS *m/z* = 249 (M$^+$); Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.74; H, 5.99.

For (*Z*)-**3p**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.07 (s, PhCH=), 7.55-7.10 (m, 15H, Ph), 7.38 (d, *J* = 12.8 Hz, =CH), 5.71 (d, *J* = 12.8 Hz, =CH); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$) δ 164.8

(Ph*C*O$_2$), 143.1, 135.8, 134.4, 134.2, 134.0, 131.4, 131.2, 130.0, 129.9, 129.3, 129.2, 128.6, 128.4, 128.3 and 127.2 (C$_{Ar}$ and =CH), 112.4 (PhCH=); GC-MS *m/z* = 326 (M$^+$).

For (*Z*)-**3r**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.65-7.24 (m, 5H, Ph), 7.38 (d, *J* = 12.8 Hz, =CH), 5.73 (d, *J* = 12.8 Hz, =CH), 2.54 (m, CO$_2$C*H*CH$_2$), 2.07-1.83 (m, 4H, C*H*$_2$CHC*H*$_2$CO$_2$), 1.78-1.24 (m, 6H, CH$_2$); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$) δ 172.7 (Ph*C*O$_2$), 134.4, 134.2, 129.2, 128.6, 128.4 and 127.2 (C$_{Ar}$ and =CH), 111.8 (=CH), 43.4 (*C*HCO$_2$), 29.1 (*C*H$_2$CHCO$_2$), 25.8 and 25.5 (CH$_2$); GC-MS *m/z* = 230 (M$^+$); Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.22; H, 7.87. Found: C, 78.39; H, 7.88.

For (*Z*)-**3s**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.65-7.20 (m, 5H, Ph), 7.15 (d, *J* = 12.8 Hz, =CH), 5.71 (d, *J* = 12.8 Hz, =CH), 2.55 (t, CO$_2$C*H*$_2$CH$_2$), 1.75 (m, CO$_2$CH$_2$C*H*$_2$), 1.50-1.15 (m, 24H, CH$_2$), 0.90 (t, CH$_3$); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ 170.5 (Ph*C*O$_2$CH), 134.4, 134.2, 129.3, 128.6 and 127.4 (C$_{Ar}$ and =CH), 111.8 (=CH), 34.4, 32.1, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 24.9 and 22.9 (CH$_2$), 14.3 (CH$_3$); GC-MS *m/z* = 358 (M$^+$).

For (*E*)-**3b**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.05-7.05 (m, 9H, Ph), 7.98 (d, *J* = 12.8 Hz, =CH), 6.47 (d, *J* = 12.8 Hz, =CH), 2.25 (s, CH$_3$); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ 163.7 (Ph*C*O$_2$), 137.4, 135.9, 133.7, 133.6, 131.1, 130.0, 129.5, 129.0 and 128.6 (C$_{Ar}$ and =CH), 115.8 (Ph*C*H=), 21.3 (CH$_3$); GC-MS *m/z* = 238 (M$^+$).

For (*E*)-**3c**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.05-7.10 (m, 10H, Ph), 8.05 (d, *J* = 12.8 Hz, =CH), 5.76 (d, *J* = 12.8 Hz, =CH); ^{13}C {^{1}H} NMR (75 MHz, CDCl$_3$) δ 163.7 (Ph*C*O$_2$), 136.1, 133.7, 133.5, 130.1 130.0, 128.9, 128.6 127.5, 126.3 and 115.9 (C$_{Ar}$ and =CH); GC-MS *m/z* = 224 (M$^+$).

For (*E*)-**3d**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.15-7.24 (m, 9H, Ph), 8.09 (d, *J* = 12.8 Hz, =CH), 6.53 (d, *J* = 12.8 Hz, =CH); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$) δ 163.7 (Ph*C*O$_2$), 137.4, 134.7, 134.0, 133.2, 132.0, 130.9, 130.2, 128.8, 127.9 and 111.5 (C$_{Ar}$ and =CH); GC-MS *m/z* = 303 (M$^+$).

For (*E*)-**3f:** ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.12-7.00 (m, 9H, Ph), 8.03 (d, *J* = 12.8 Hz, =CH), 6.56 (d, *J* = 12.8 Hz, =CH); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ 163.8 (Ph*C*O$_2$), 163.6, 161.2, 136.3, 134.0, 130.3, 129.0, 128.0, 127.9, 116.0 (C$_{Ar}$ and =CH) and 115.0 (C$_{Ar}$ and =CH); GC-MS *m/z* = 242 (M$^+$); Calcd for $C_{15}H_{11}FO_2$: C, 74.37; H, 4.58. Found: C, 73.27; H, 4.50.

For **4a:** ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.08-7.38 (m, 5H, Ph), 4.84 (s, 2H, PhCO$_2$C*H*$_2$), 2.18 (s, COCH$_3$); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$) δ 201.9 (*C*OCH$_3$), 165.9 (Ph*C*O$_2$), 133.5, 129.9, 129.2 and 128.5 (C$_{Ar}$), 68.8 (PhCO$_2$*C*H$_2$), 26.6 (CO*C*H$_3$); GC-MS *m/z* = 178 (M$^+$).

For **4b:** ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.10-7.38 (m, 5H, Ph), 5.29 (m, PhCO$_2$C*H*), 2.22 (s, COCH$_3$), 1.53 (d, *J* = 7.1 Hz, PhCO$_2$CHC*H*$_3$); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$) δ 205.9 (*C*OCH$_3$), 165.9 (Ph*C*O$_2$), 133.5, 129.9, 129.5 and 128.5 (C$_{Ar}$), 75.6 (CO$_2$*C*H), 25.8 (CO*C*H$_3$), 16.2 (CO$_2$CH*C*H$_3$); GC-MS *m/z* = 192 (M$^+$).

For **4c:** ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.10-7.38 (m, 5H, Ph), 2.12 (s, COC*H*$_3$), 1.55 (s, 6H, PhCO$_2$C(C*H*$_3$)$_2$); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$) δ 206.7 (*C*OCH$_3$), 165.9 (Ph*C*O$_2$), 133.5, 129.7, 129.5 and 128.5 (C$_{Ar}$), 84.2 (=*C*Ph), 23.6 (CO*C*H$_3$), 23.4 (CO$_2$C(*C*H$_3$)$_2$); GC-MS *m/z* = 206 (M$^+$).

For **4d:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10-7.38 (m, 5H, Ph), 2.14 (m, 2H), 2.06 (s, 3H, $COCH_3$), 1.74-1.50 (m, 8H, CH_2 and CH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 206.9 (*C*OCH_3), 165.9 (Ph*C*O_2), 133.3, 129.7, 129.5 and 128.5 (C_{Ar}), 85.5 (=*C*Ph), 30.8, 25.5, 23.5 and 21.3 (CH_2 and CH_3); GC-MS *m/z* = 247 (M^+).

For **4f:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.60 (s, CO_2CH_2), 2.60 (m, 2H, CH_2CO_2), 2.40 (s, $COCH_3$), 2.15 (m, 26H, CH_2), 0.85 (t, CH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 201.8 (*C*OCH_3), 175.2 (*C*O_2), 68.3 (CO*C*H_2CO_2), 51.9 (CO*C*H_2), 34.1, 34.0, 32.1, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 26.2, and 22.9 (CH_2), 25.0 (CO*C*H_3), 14.3 (CH_2*C*H_3); GC-MS *m/z* = 276 (M^+).

For **4g:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.60 (s, 2H, CO_2CH_2), 2.40 (m, $CHCO_2$), 2.13 (s, $COCH_3$), 2.0-1.10 (m, 10H, CH_2); ^{13}C $\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 202.2 (*C*OCH_3), 175.5 (*C*O_2), 68.2 (CO*C*H_2CO_2), 42.9 (CO*C*H), 29.1, 26.3 and 25.5 (CH_2), 25.9 (CO*C*H_3); GC-MS *m/z* = 184 (M^+).

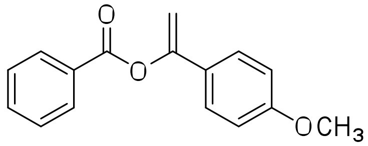
For **4h:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (s, CHPh), 7.40-7.08 (m, 10H, Ph), 4.75 (s, 2H, CO_2CH_2), 2.10 (s, $COCH_3$); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 201.6 (*C*OCH_3), 166.8 (*C*O_2), 141.4, 135.4, 134.3, 131.5, 130.6, 129.9, 129.2, 128.5, 128.1 and 127.8 (C_{Ar} and C_{vinyl}) 68.8 (CO*C*H_2CO_2), 25.9 (CO*C*H_3); GC-MS *m/z* = 280 (M^+).

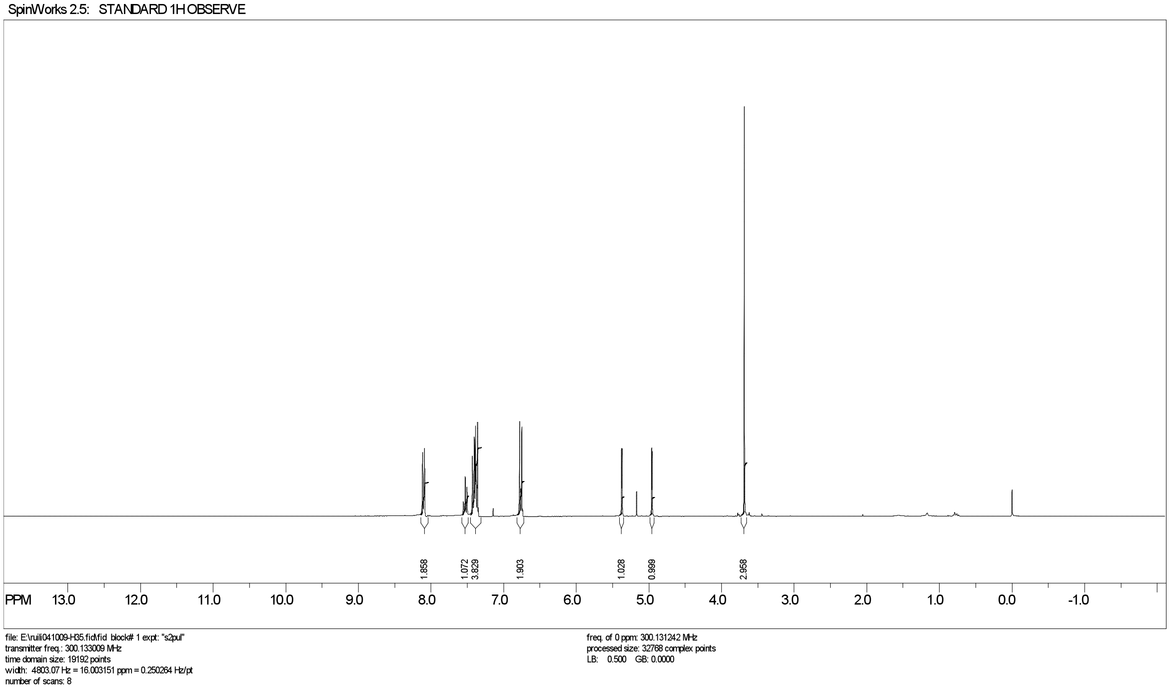
For **5a:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25-7.45 (m, 14H, Ph), 5.6 (d, *J* = 2.4 Hz, 2H, CO_2C*H_2*), 5.22 (d, *J* = 2.4 Hz, 2H, C*H_2*CO_2); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 164.9 (CO_2), 152.7, 135.0, 133.8, 130.3, 129.4, 128.8 and 125.3 (C_{Ar} and =C), 103.1 (=CH_2); GC-MS *m/z* = 370 (M^+).

For **5b:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10-7.35 (m, 10H, Ph), 4.91 (d, *J* = 2.4 Hz, 4H, $PhCO_2CH_2$), 2.45 (t, *J* = 7.5 Hz, 4H, $CO_2CH_2CH_2$), 1.78 (m, 2H, $PhCO_2CH_2CH_2CH_2$); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 164.7 (CO_2), 155.8, 133.4, 130.0, 129.8 and 128.5 (C_{Ar} and =C), 102.2 (=CH_2), 32.7 (=CH_2CH_2), 23.5 (=$CH_2CH_2CH_2$); GC-MS *m/z* = 336 (M^+).

The ^{1}H and ^{13}C NMR Spectra of Selected Organic Products

2a

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number of scans: 8

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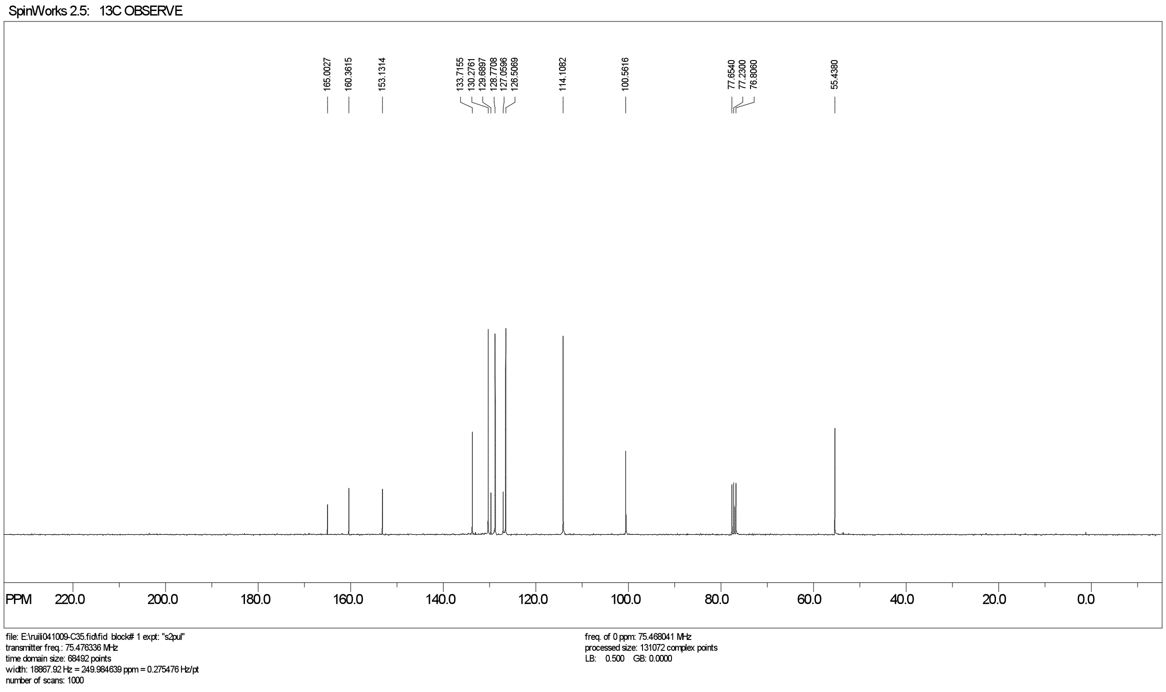
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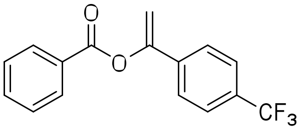
2e



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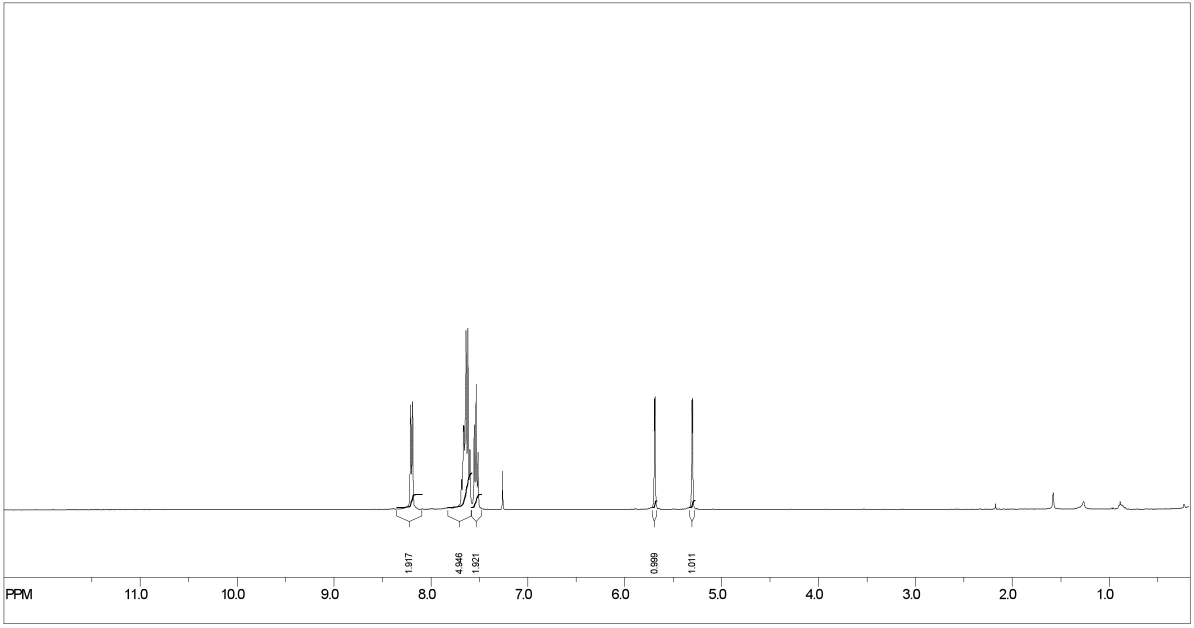

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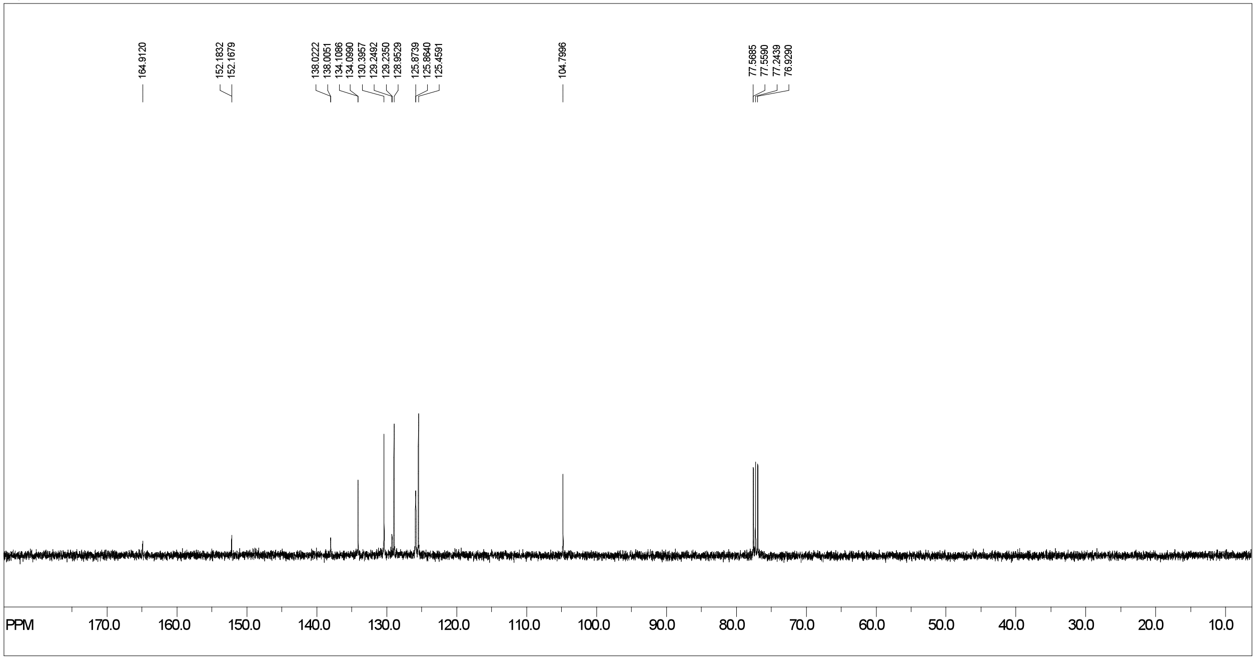

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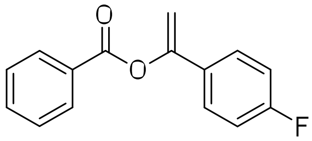
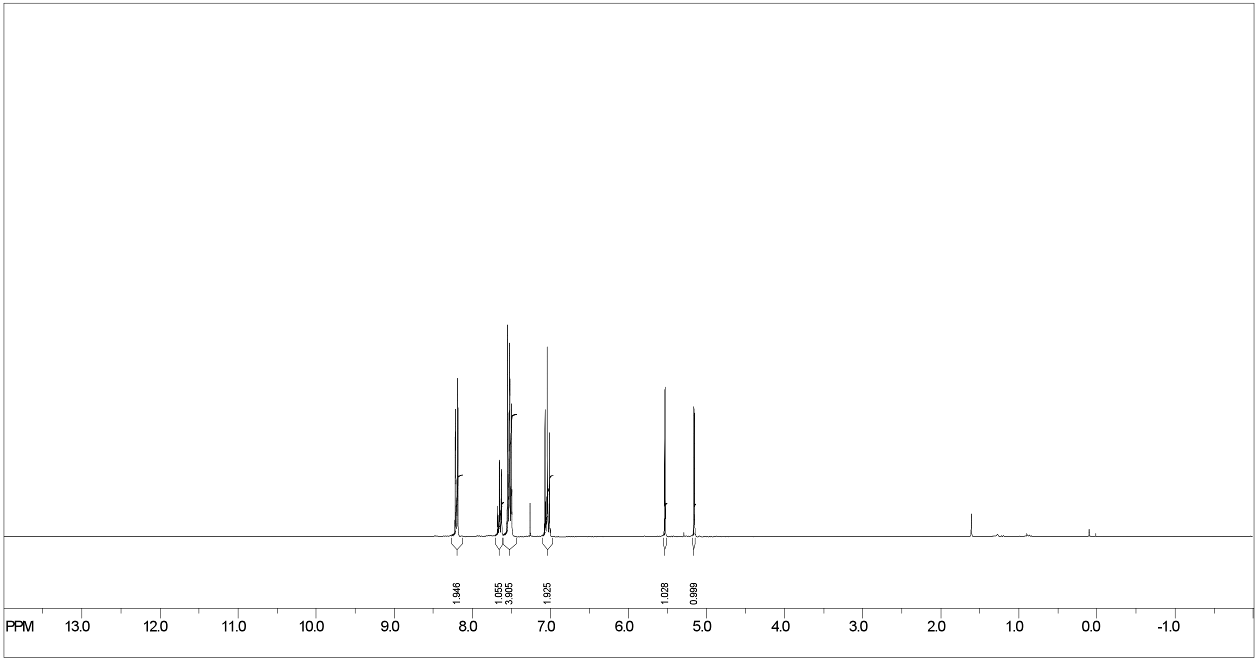
2f



SpinWorks 2.5: STANDARD 1H OBSERVE



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number of scans: 8

freq. of 0 ppm: 300.131208 MHz
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LB: 0.000 GB: 0.0000

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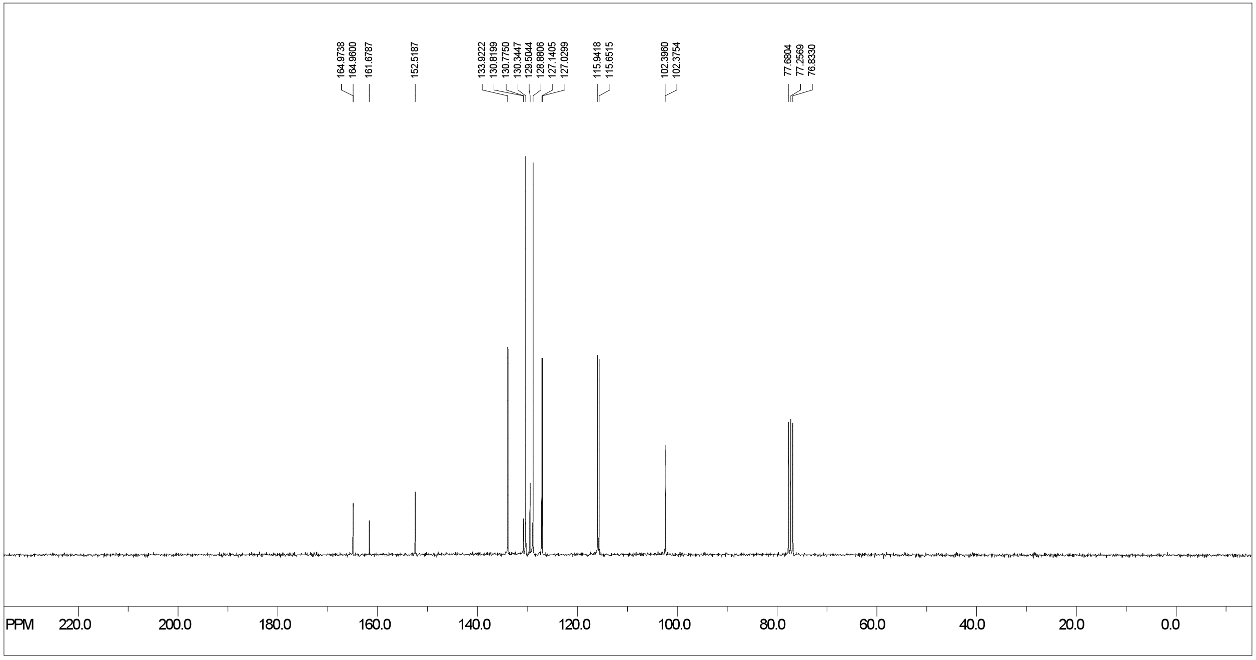

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number of scans: 1100

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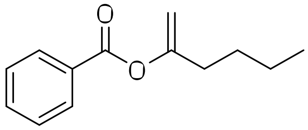
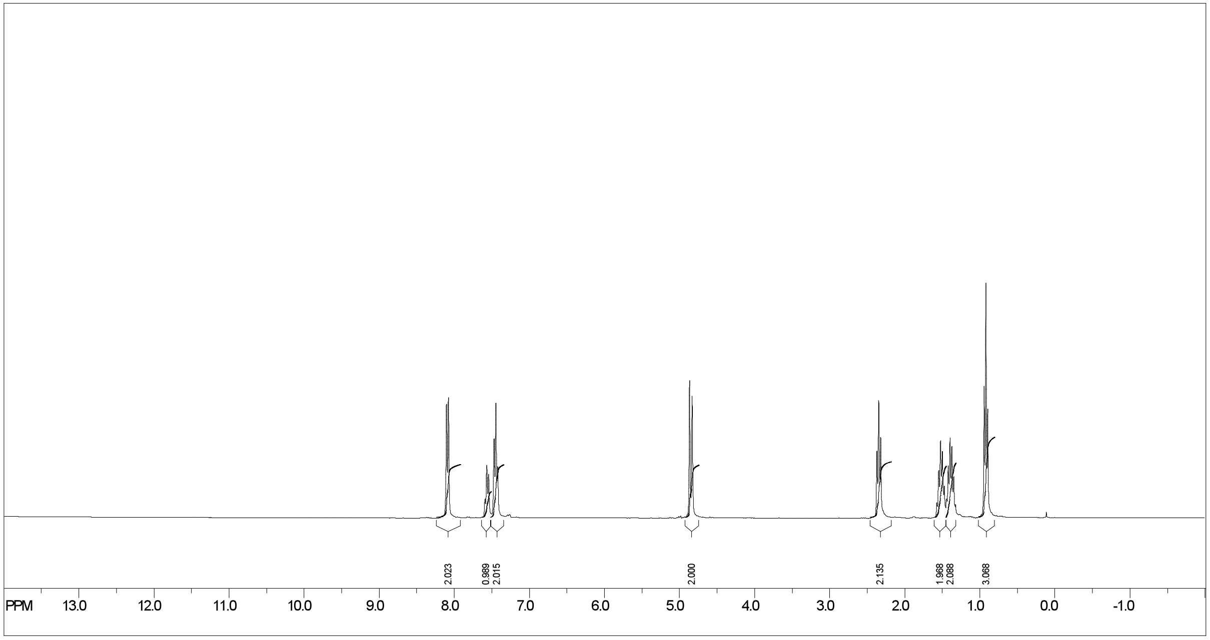


2g

SpinWorks 2.5: STANDARD 1H OBSERVE



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number of scans: 8

freq. of 0 ppm: 300.131208 MHz
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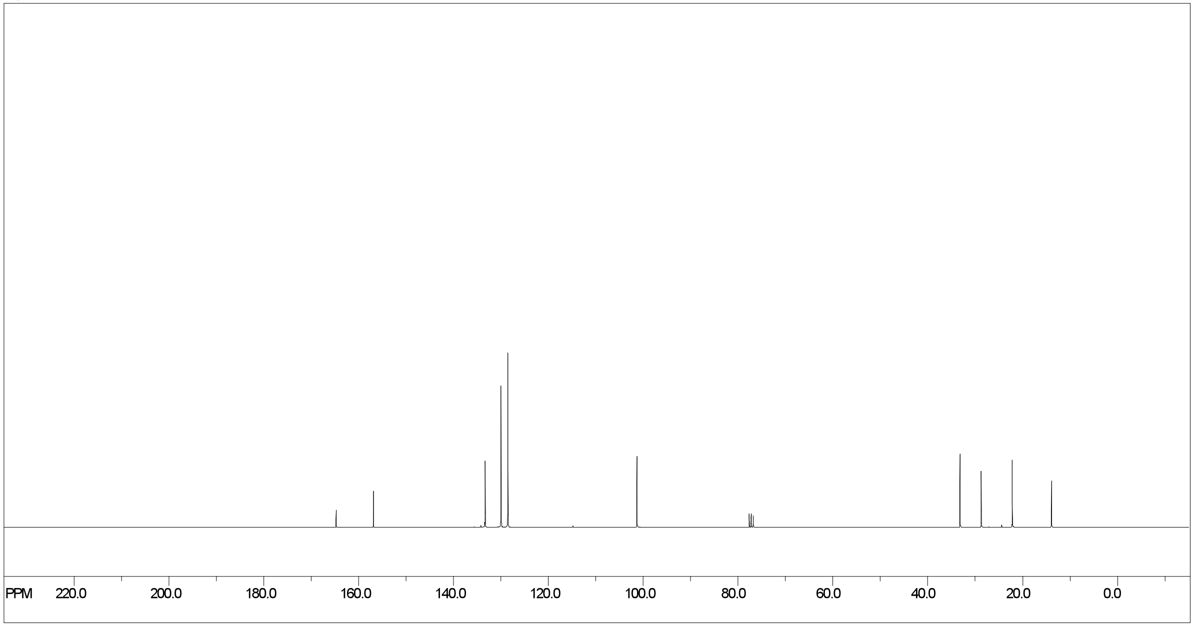
LB: 0.000 GB: 0.0000

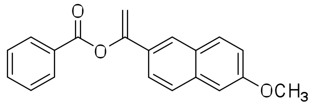
SpinWorks 2.5: 13C OBSERVE

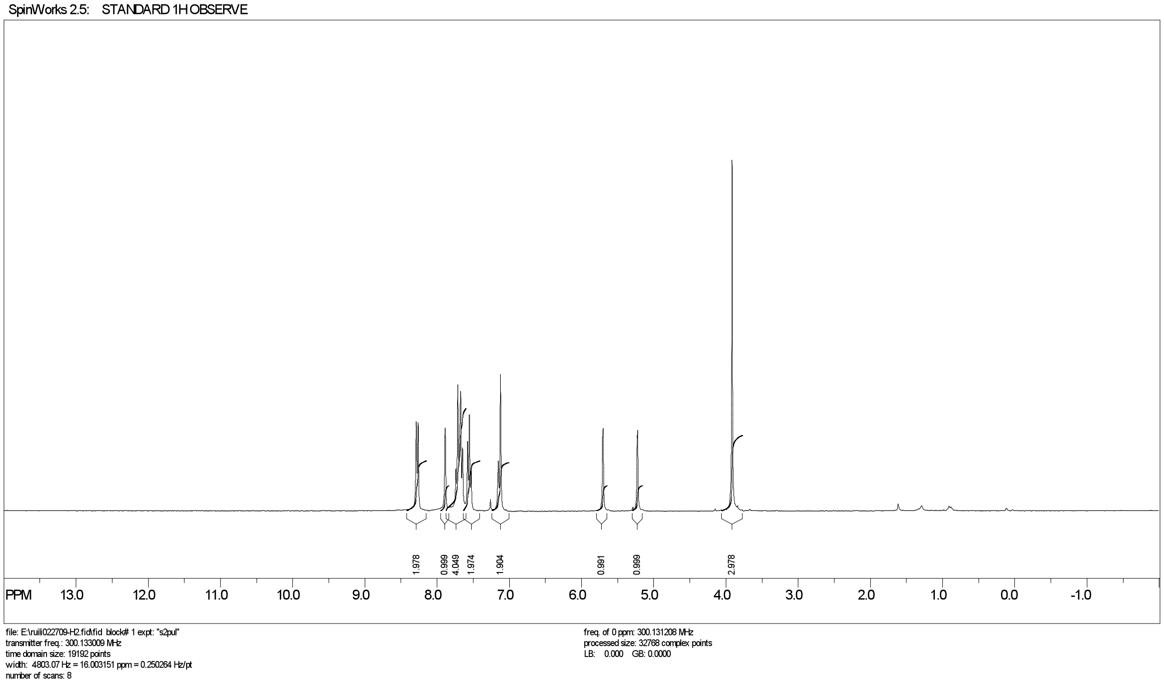


file: E:\ruili022709C5.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 75.476336 MHz
time domain size: 68492 points
width: 18867.92 Hz = 249.984639 ppm = 0.275476 Hz/pt
number of scans: 0

freq. of 0 ppm: 75.468046 MHz
processed size: 16384 complex points
LB: 0.000 GB: 0.0000

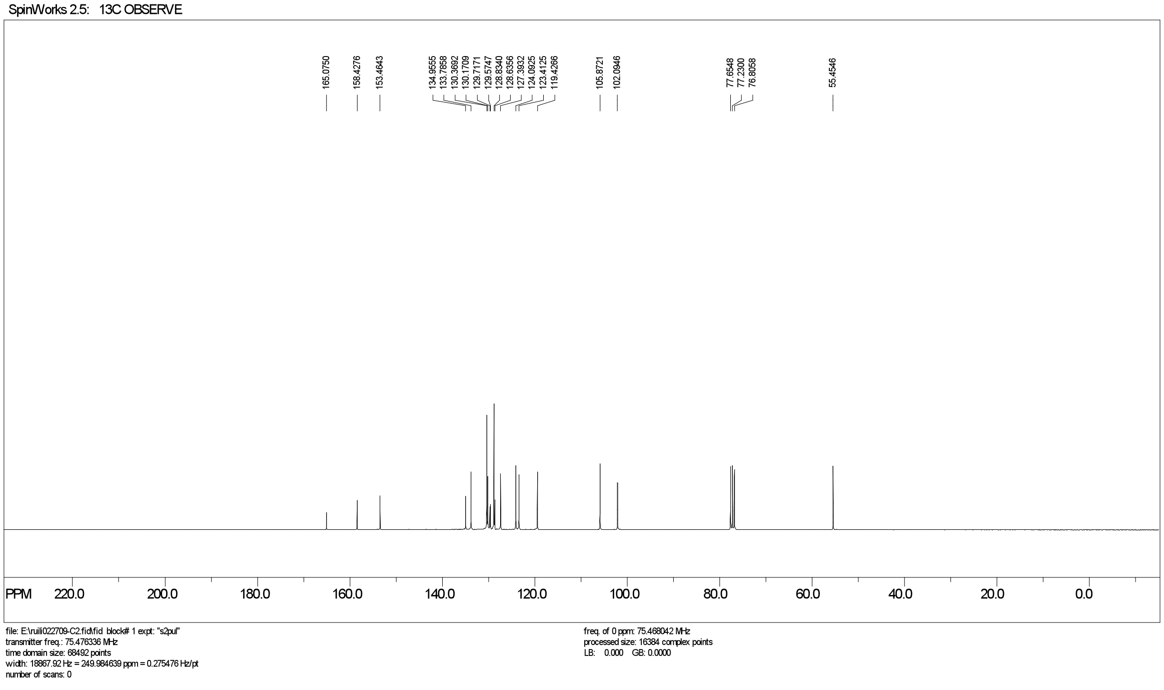
2j





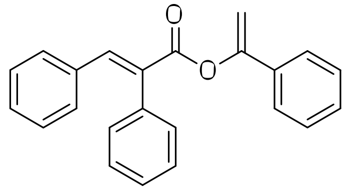
```
file: E:\ruili022709-H2.fid\fid  block# 1 expt: "s2pul"
transmitter freq.: 300.133009 MHz
time domain size: 19192 points
width:  4803.07 Hz = 16.003151 ppm = 0.250264 Hz/pt
number of scans: 8
```

```
freq. of 0 ppm: 300.131208 MHz
processed size: 32768 complex points
LB:    0.000    GB: 0.0000
```



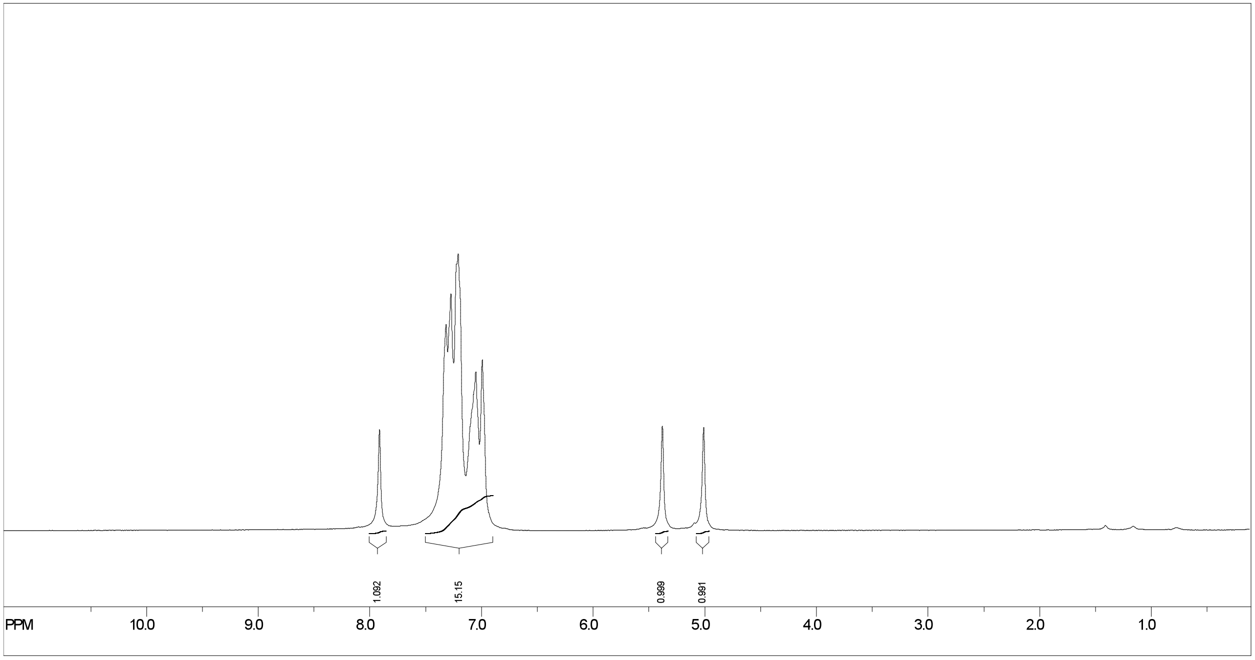
```
file: E:\ruili022709-C2.fid\fid  block# 1 expt: "s2pul"
transmitter freq.: 75.476336 MHz
time domain size: 68492 points
width: 18867.92 Hz = 249.984639 ppm = 0.275476 Hz/pt
number of scans: 0
```

```
freq. of 0 ppm: 75.468042 MHz
processed size: 16384 complex points
LB:    0.000    GB: 0.0000
```



2p

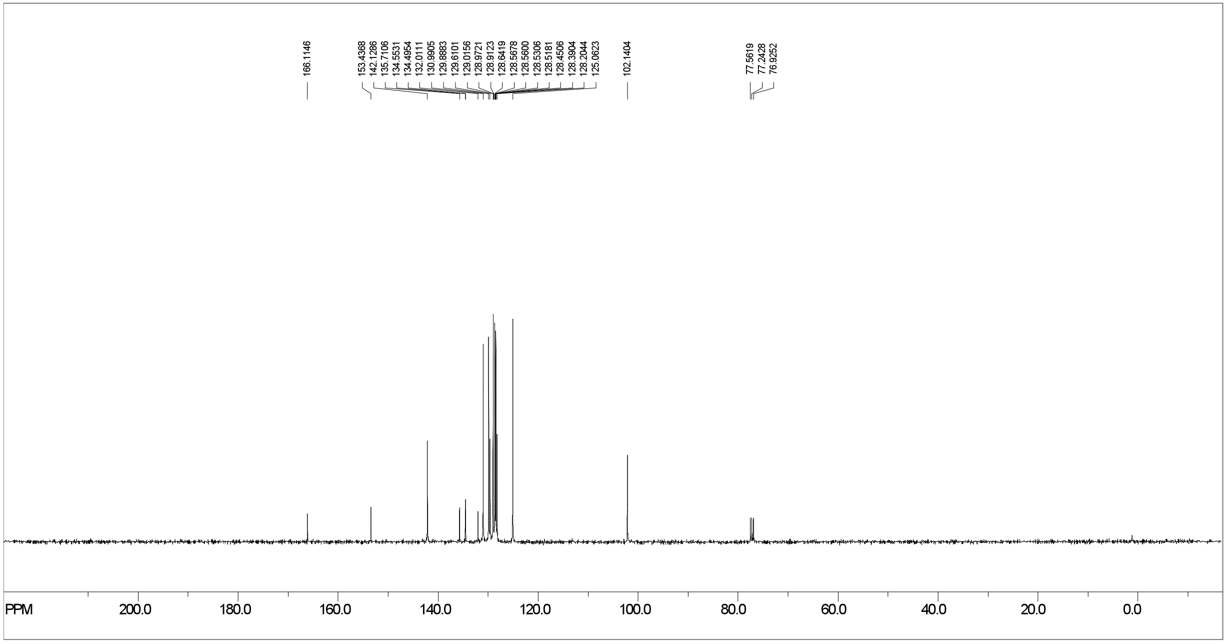
SpinWorks 2.5:



file: E:\030909-H12.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 399.751086 MHz
time domain size: 26264 points
width: 6410.26 Hz = 16.035620 ppm = 0.244070 Hz/pt
number of scans: 8

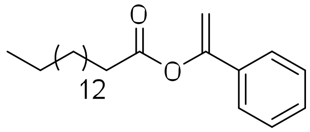
freq. of 0 ppm: 399.748758 MHz
processed size: 65536 complex points
LB: 0.000 GB: 0.0000

SpinWorks 2.5:



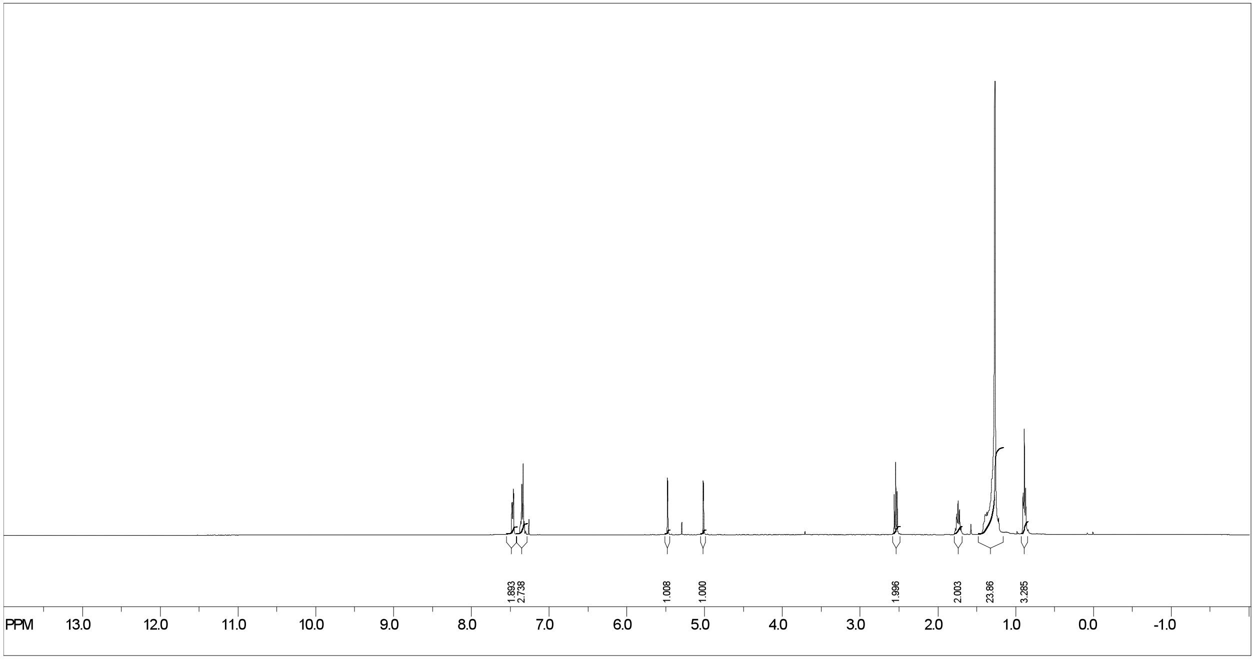
file: E:\030909-C12.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 100.527442 MHz
time domain size: 63750 points
width: 24509.80 Hz = 243.812072 ppm = 0.384468 Hz/pt
number of scans: 256

freq. of 0 ppm: 100.516881 MHz
processed size: 65536 complex points
LB: 0.000 GB: 0.0000



2s

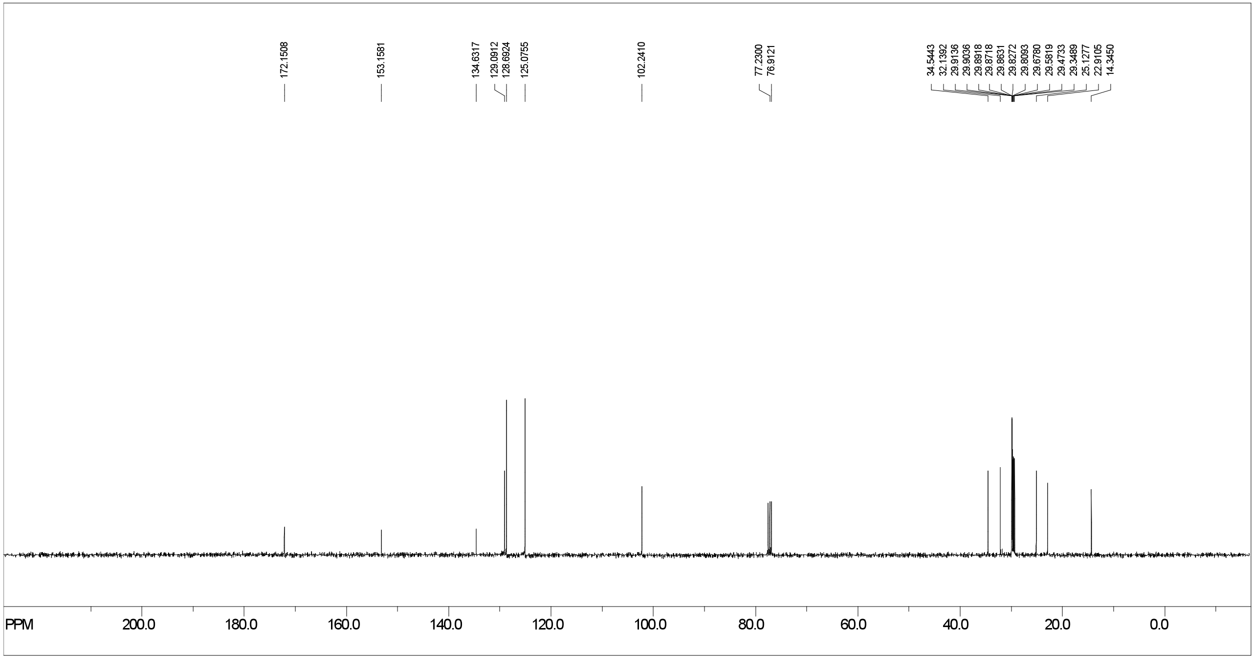
SpinWorks 2.5:



file: E:\031109H17.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 399.751086 MHz
time domain size: 26264 points
width: 6410.26 Hz = 16.035620 ppm = 0.244070 Hz/pt
number of scans: 8

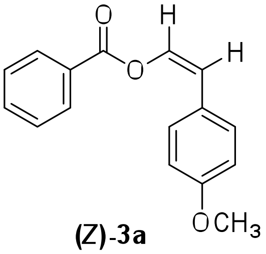
freq. of 0 ppm: 399.748687 MHz
processed size: 65536 complex points
LB: 0.000 GB: 0.0000

SpinWorks 2.5:



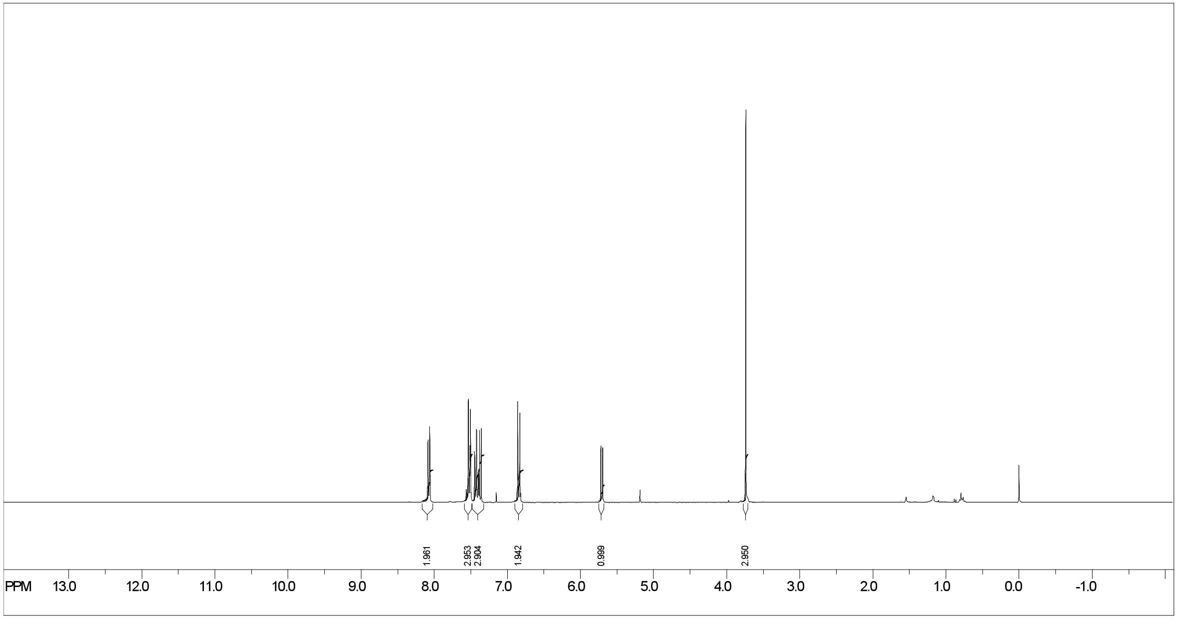
file: E:\031109C17.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 100.527442 MHz
time domain size: 63750 points
width: 24509.80 Hz = 243.812072 ppm = 0.384468 Hz/pt
number of scans: 256

freq. of 0 ppm: 100.516867 MHz
processed size: 65536 complex points
LB: 0.500 GB: 0.0000



(Z)-3a

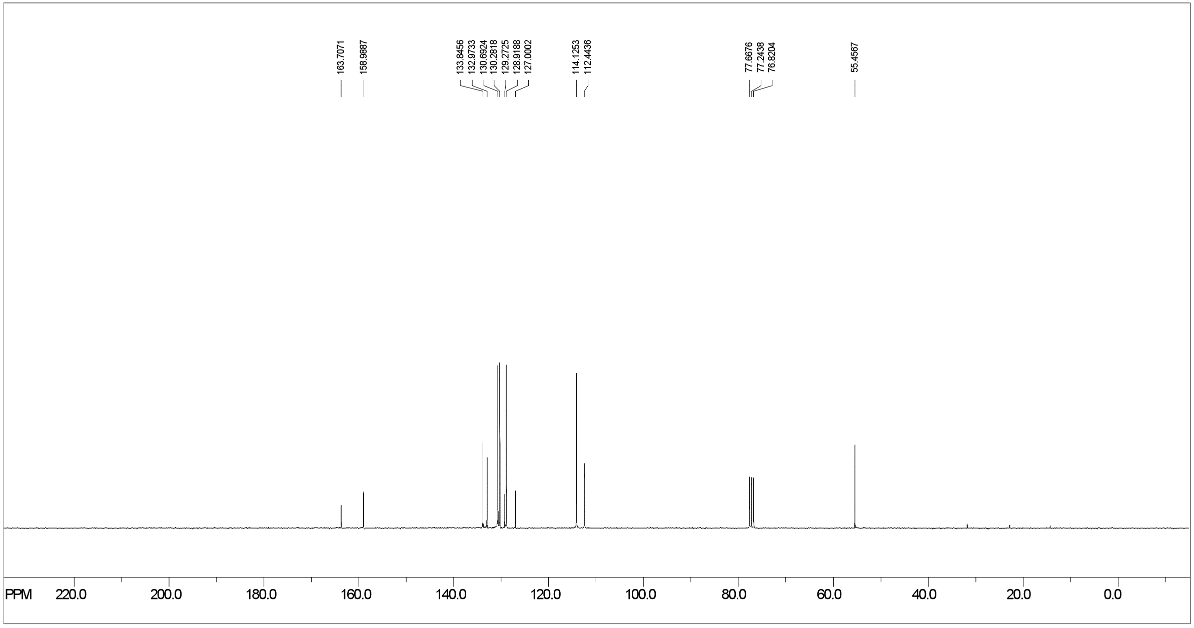
SpinWorks 2.5: STANDARD 1H OBSERVE



file: E:\ruili040809-H34.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 300.133009 MHz
time domain size: 19192 points
width: 4803.07 Hz = 16.003151 ppm = 0.250264 Hz/pt
number of scans: 8

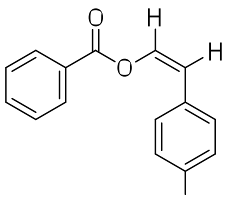
freq. of 0 ppm: 300.131240 MHz
processed size: 32768 complex points
LB: 0.500 GB: 0.0000

SpinWorks 2.5: 13C OBSERVE



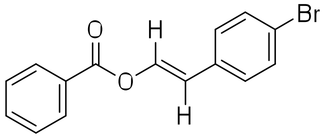
file: E:\ruili040809-C34.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 75.476336 MHz
time domain size: 68492 points
width: 18867.92 Hz = 249.984639 ppm = 0.275476 Hz/pt
number of scans: 1088

freq. of 0 ppm: 75.468039 MHz
processed size: 131072 complex points
LB: 0.500 GB: 0.0000



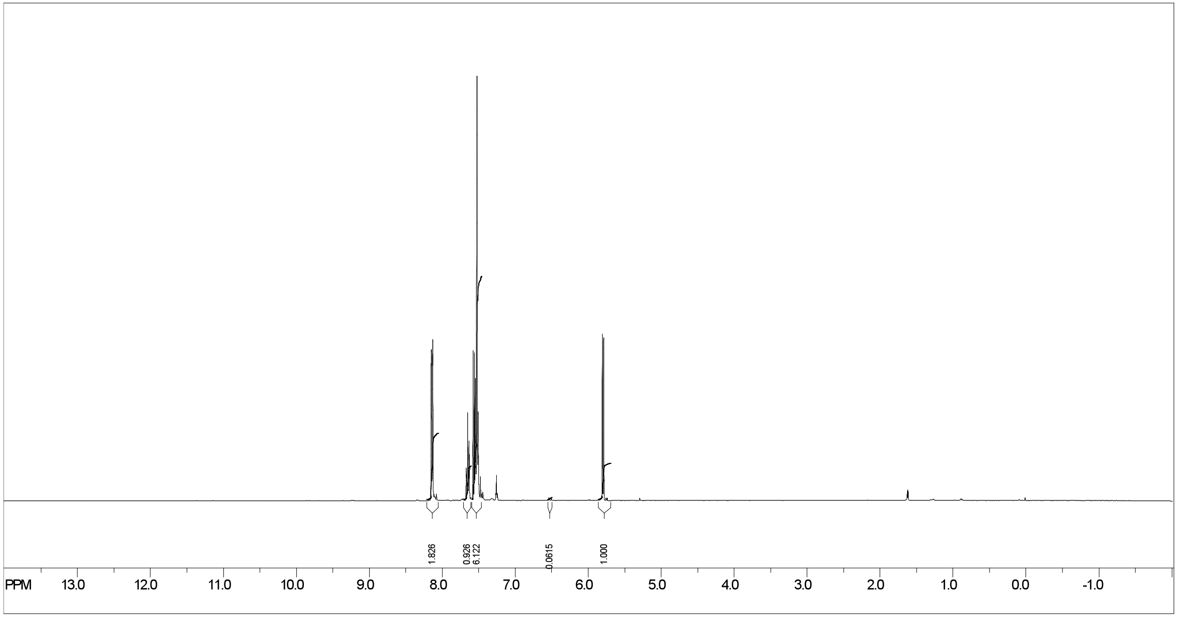
(*Z*)-3d

+



(*E*)-3d

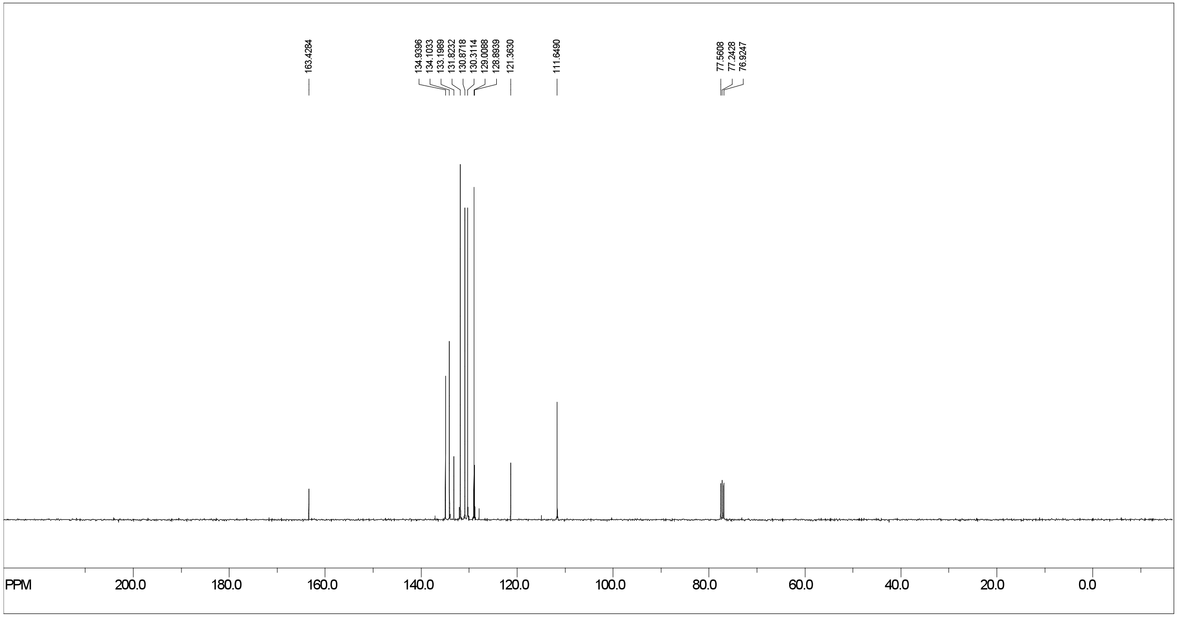
SpinWorks 2.5:



file: E:\031609-H19.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 399.751086 MHz
time domain size: 26264 points
width: 6410.26 Hz = 16.035620 ppm = 0.244070 Hz/pt
number of scans: 8

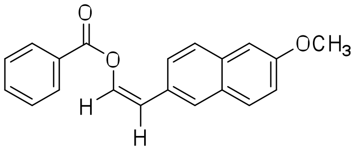
freq. of 0 ppm: 399.748688 MHz
processed size: 65536 complex points
LB: 0.500 GB: 0.0000

SpinWorks 2.5:



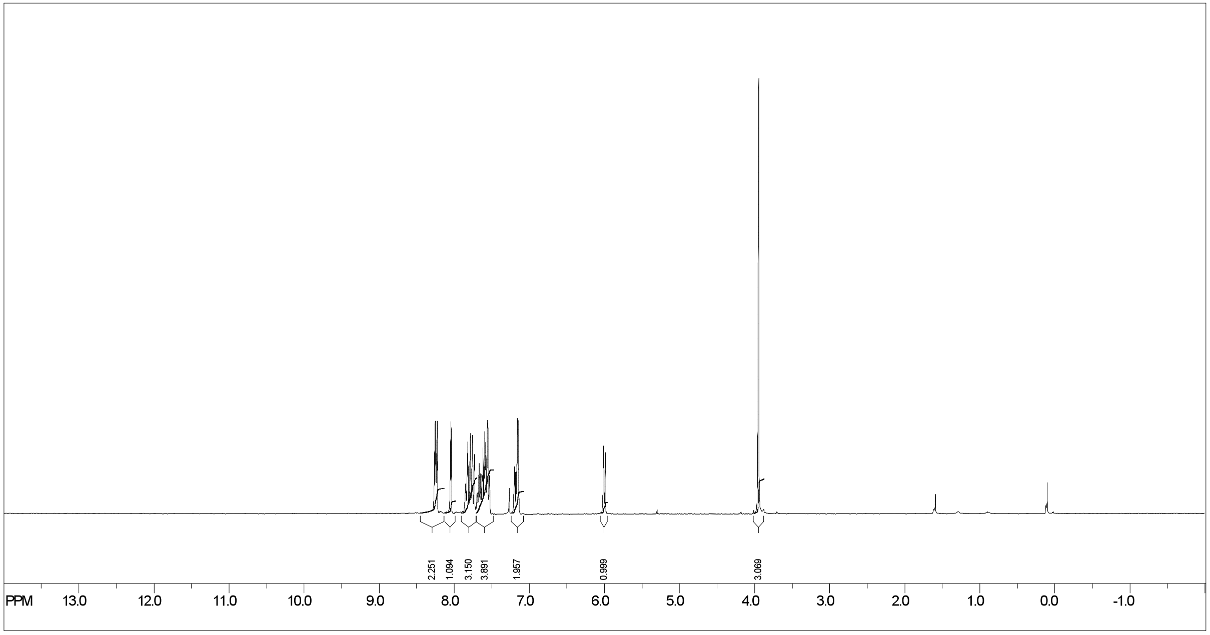
file: E:\031609-C19.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 100.527442 MHz
time domain size: 63750 points
width: 24509.80 Hz = 243.812072 ppm = 0.384468 Hz/pt
number of scans: 704

freq. of 0 ppm: 100.516870 MHz
processed size: 65536 complex points
LB: 0.500 GB: 0.0000



(*Z*)-3g

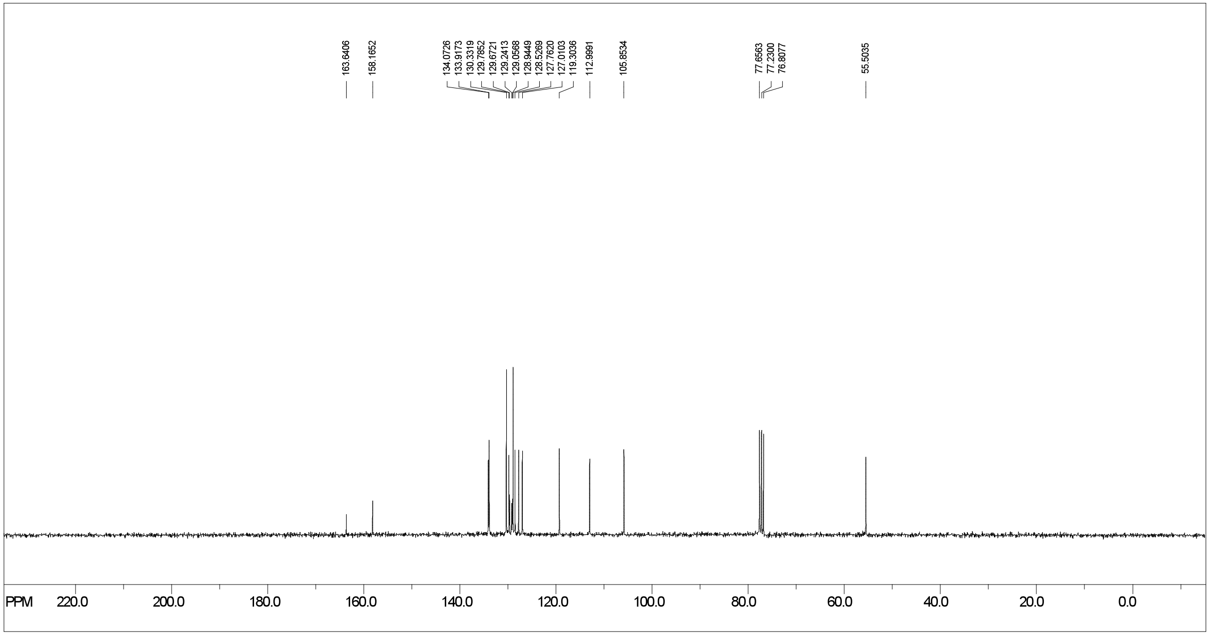
SpinWorks 2.5: STANDARD 1H OBSERVE



file: E:\ruili032309-H28.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 300.133009 MHz
time domain size: 19192 points
width: 4803.07 Hz = 16.003151 ppm = 0.250264 Hz/pt
number of scans: 8

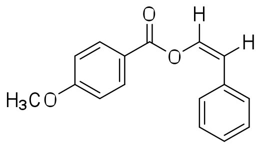
freq. of 0 ppm: 300.131208 MHz
processed size: 32768 complex points
LB: 0.000 GB: 0.0000

SpinWorks 2.5: 13C OBSERVE



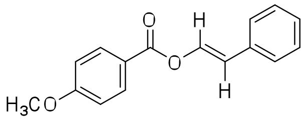
file: E:\ruili032309-C28.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 75.476336 MHz
time domain size: 68492 points
width: 18867.92 Hz = 249.984639 ppm = 0.275476 Hz/pt
number of scans: 768

freq. of 0 ppm: 75.468039 MHz
processed size: 131072 complex points
LB: 0.000 GB: 0.0000



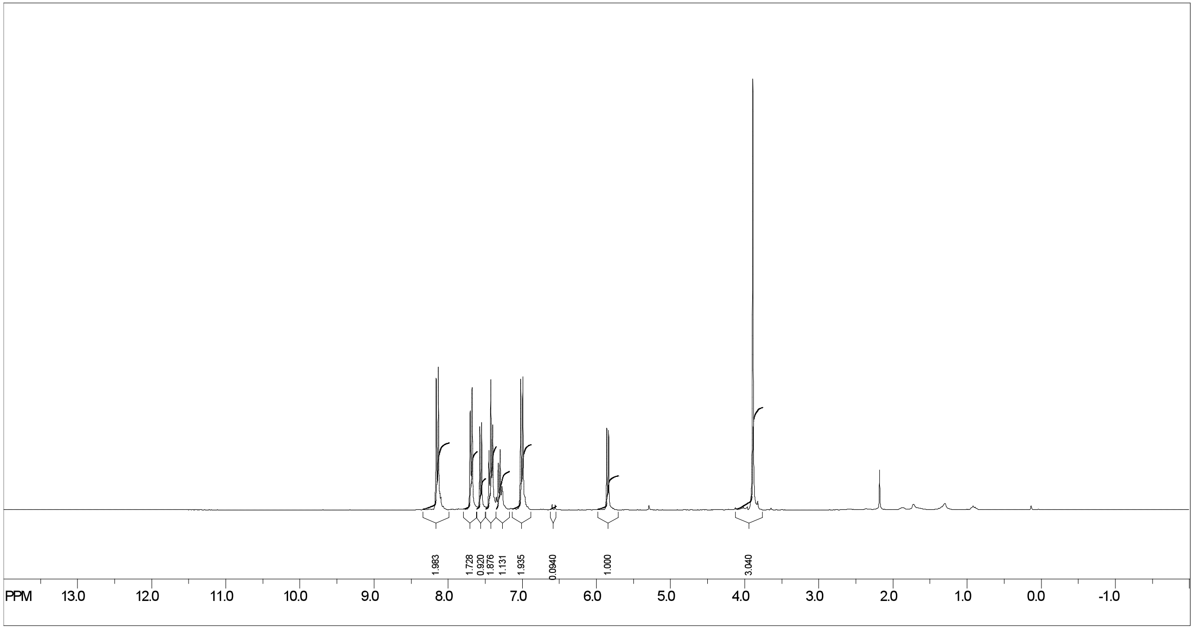
(*Z*)-3k

+



(*E*)-3k

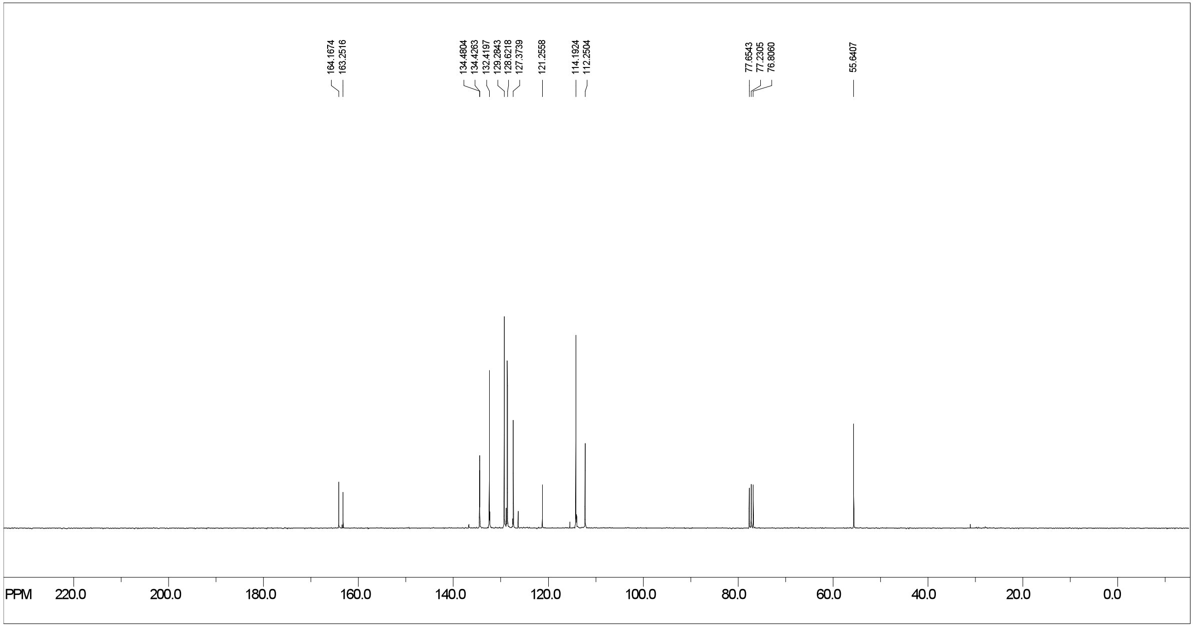
SpinWorks 2.5: STANDARD 1H OBSERVE



file: E:\ruili031709-H22.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 300.133009 MHz
time domain size: 19192 points
width: 4803.07 Hz = 16.003151 ppm = 0.250264 Hz/pt
number of scans: 8

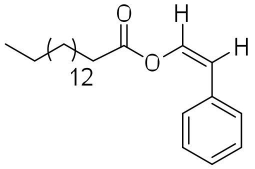
freq. of 0 ppm: 300.131208 MHz
processed size: 32768 complex points
LB: 0.000 GB: 0.0000

SpinWorks 2.5: 13C OBSERVE



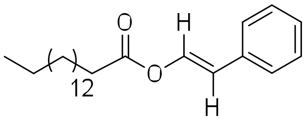
file: E:\ruili031709-C22.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 75.476336 MHz
time domain size: 68492 points
width: 18867.92 Hz = 249.984639 ppm = 0.275476 Hz/pt
number of scans: 1200

freq. of 0 ppm: 75.468044 MHz
processed size: 16384 complex points
LB: 0.000 GB: 0.0000



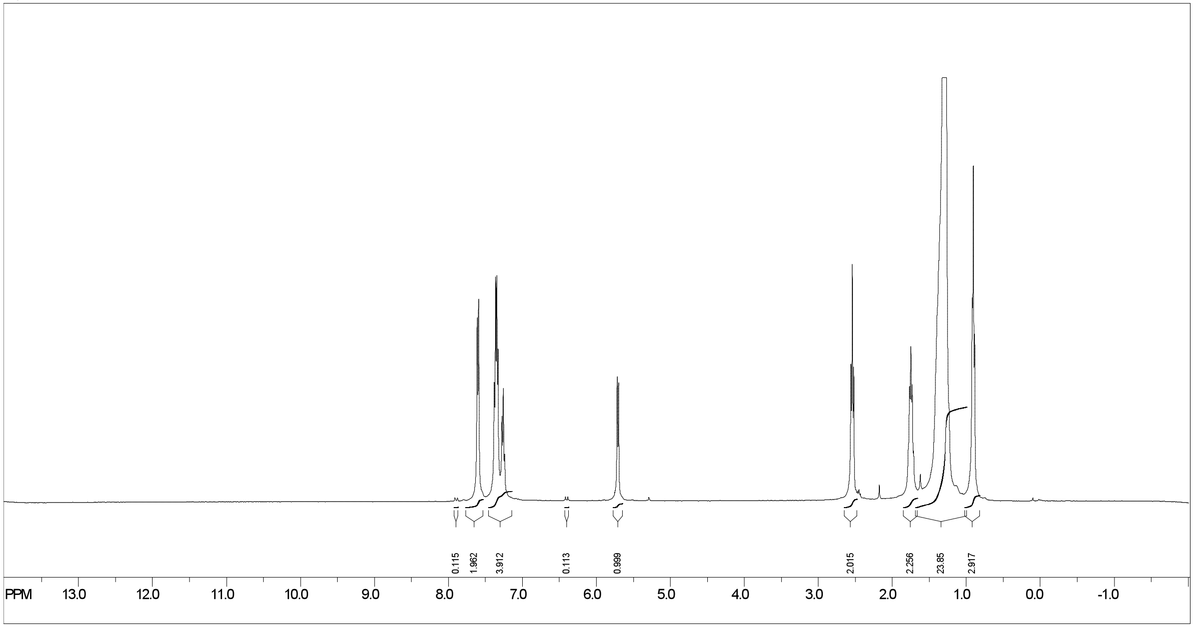
(*Z*)-3s

+



(*E*)-3s

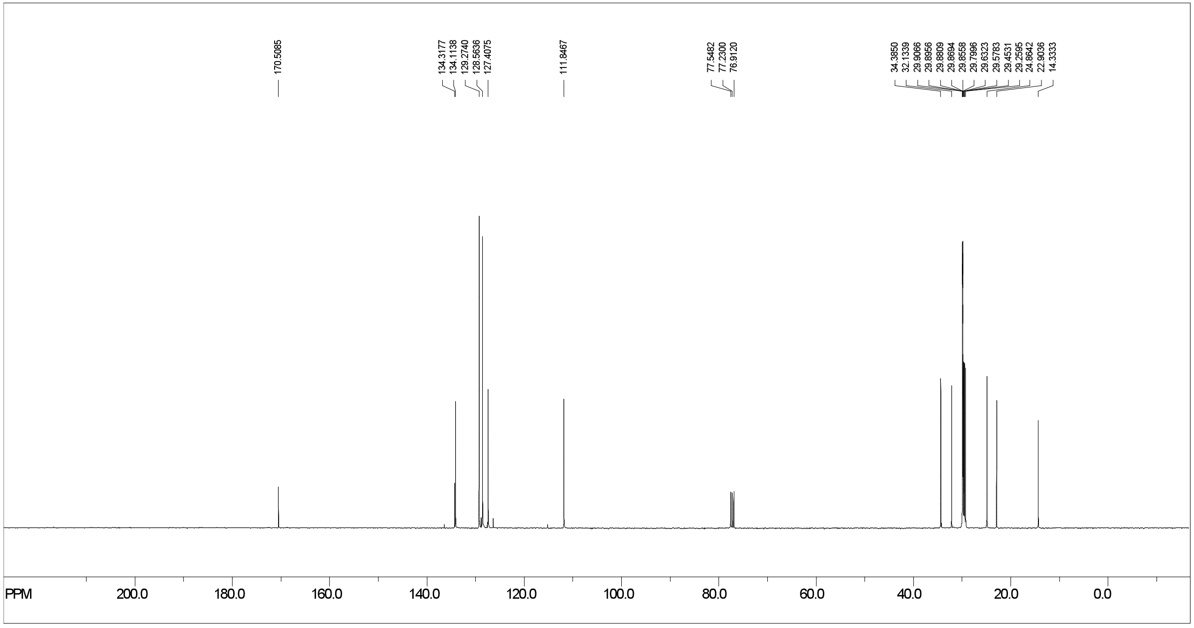
SpinWorks 2.5:



file: E:\031709-H23.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 399.751086 MHz
time domain size: 26264 points
width: 6410.26 Hz = 16.035620 ppm = 0.244070 Hz/pt
number of scans: 8

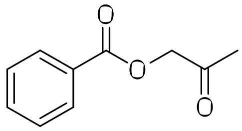
freq. of 0 ppm: 399.748688 MHz
processed size: 65536 complex points
LB: 0.500 GB: 0.0000

SpinWorks 2.5:



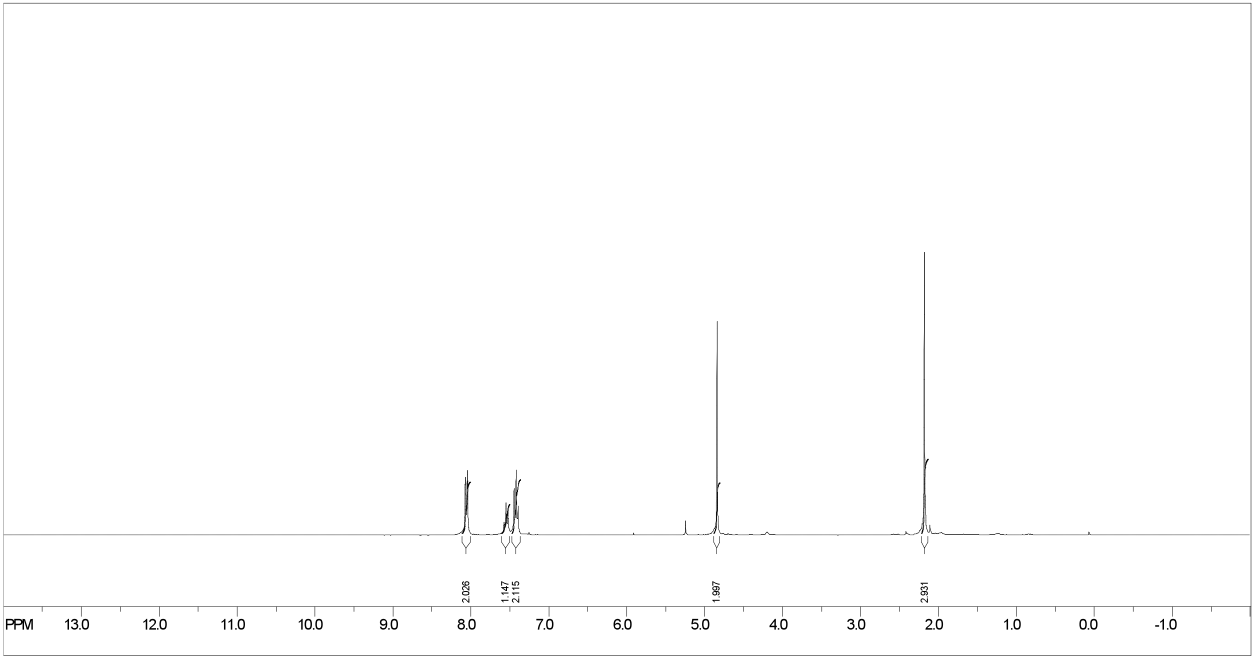
file: E:\031709-C23.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 100.527442 MHz
time domain size: 63750 points
width: 24509.80 Hz = 243.812072 ppm = 0.384468 Hz/pt
number of scans: 3600

freq. of 0 ppm: 100.516870 MHz
processed size: 65536 complex points
LB: 0.500 GB: 0.0000



4a

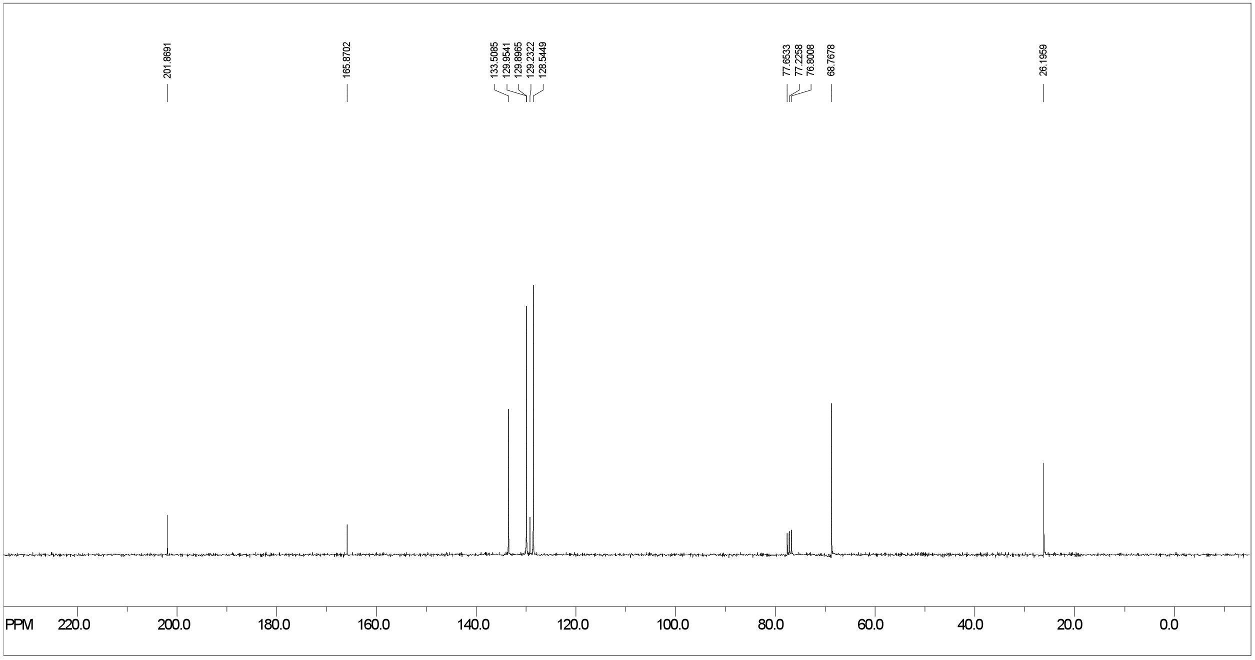
SpinWorks 2.5: STANDARD 1H OBSERVE



file: E:\ruili042909-H3.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 300.133009 MHz
time domain size: 19192 points
width: 4803.07 Hz = 16.003151 ppm = 0.250264 Hz/pt
number of scans: 8

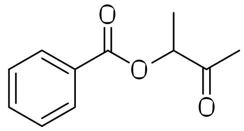
freq. of 0 ppm: 300.131208 MHz
processed size: 32768 complex points
LB: 0.500 GB: 0.0000

SpinWorks 2.5: 13C OBSERVE



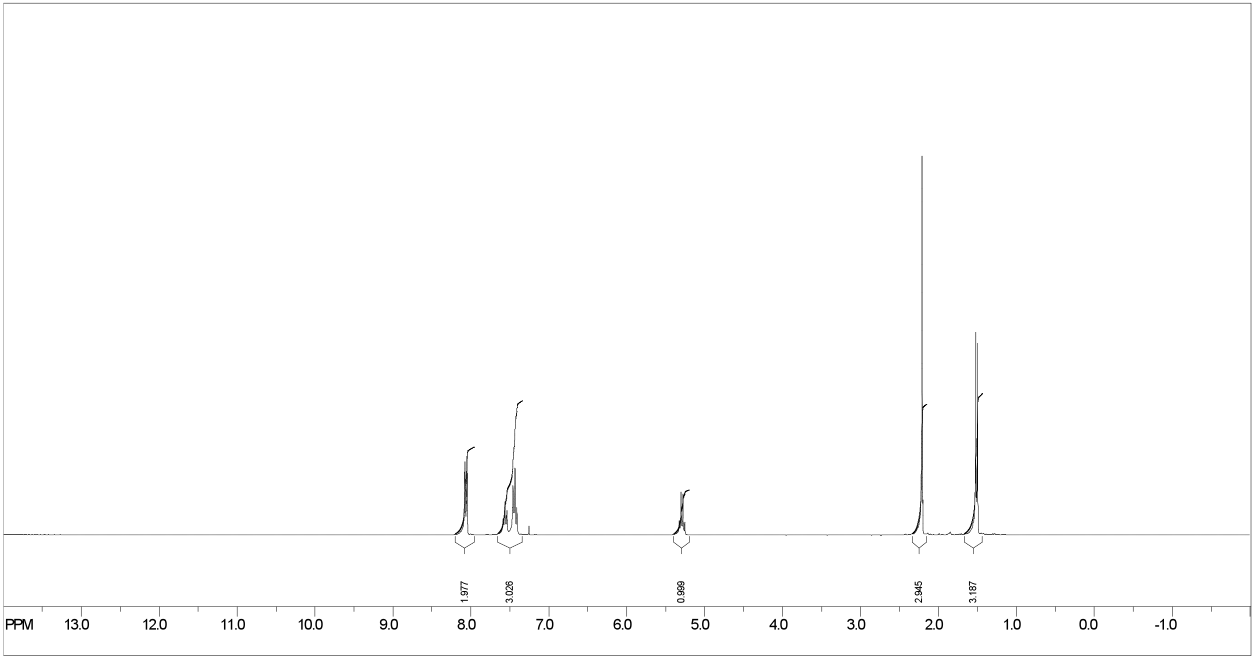
file: E:\ruili042909-C3.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 75.476336 MHz
time domain size: 68492 points
width: 18867.92 Hz = 249.984639 ppm = 0.275476 Hz/pt
number of scans: 192

freq. of 0 ppm: 75.468047 MHz
processed size: 131072 complex points
LB: 0.500 GB: 0.0000



4b

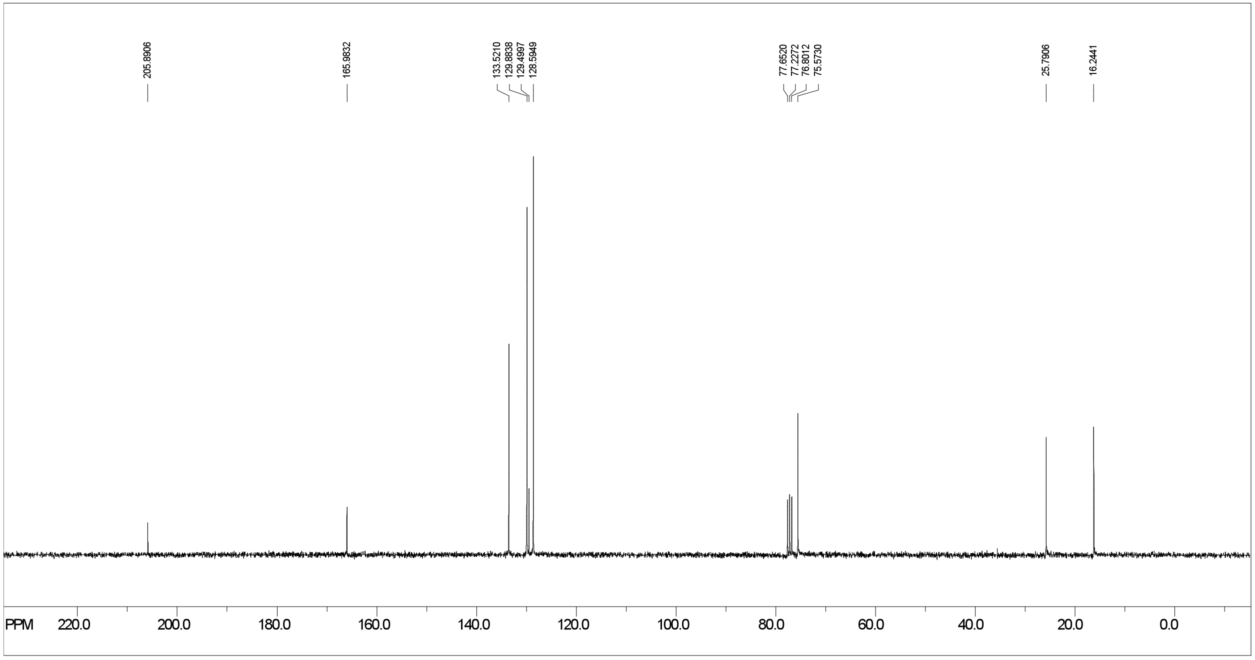
SpinWorks 2.5: STANDARD 1H OBSERVE



file: E:\ruili051209-H.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 300.133009 MHz
time domain size: 19192 points
width: 4803.07 Hz = 16.003151 ppm = 0.250264 Hz/pt
number of scans: 8

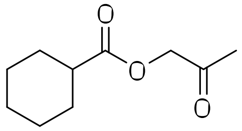
freq. of 0 ppm: 300.131208 MHz
processed size: 32768 complex points
LB: 0.500 GB: 0.0000

SpinWorks 2.5: 13C OBSERVE



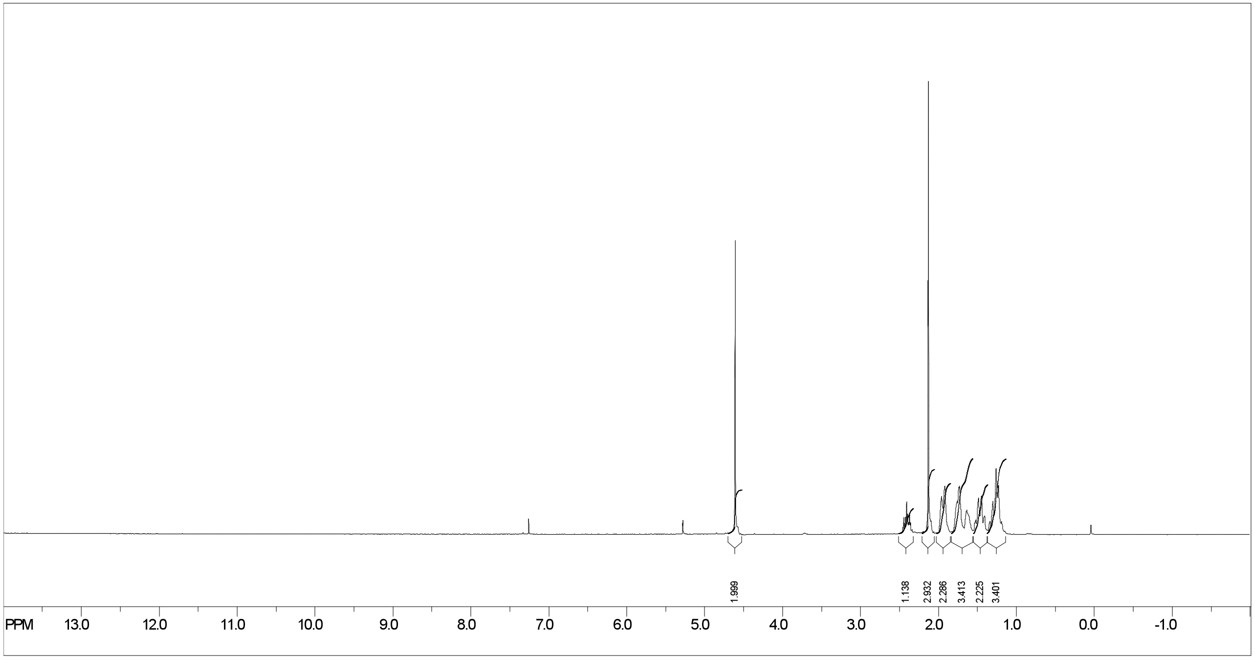
file: E:\ruili051209C.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 75.476336 MHz
time domain size: 68492 points
width: 18867.92 Hz = 249.984639 ppm = 0.275476 Hz/pt
number of scans: 256

freq. of 0 ppm: 75.468042 MHz
processed size: 131072 complex points
LB: 0.500 GB: 0.0000



4g

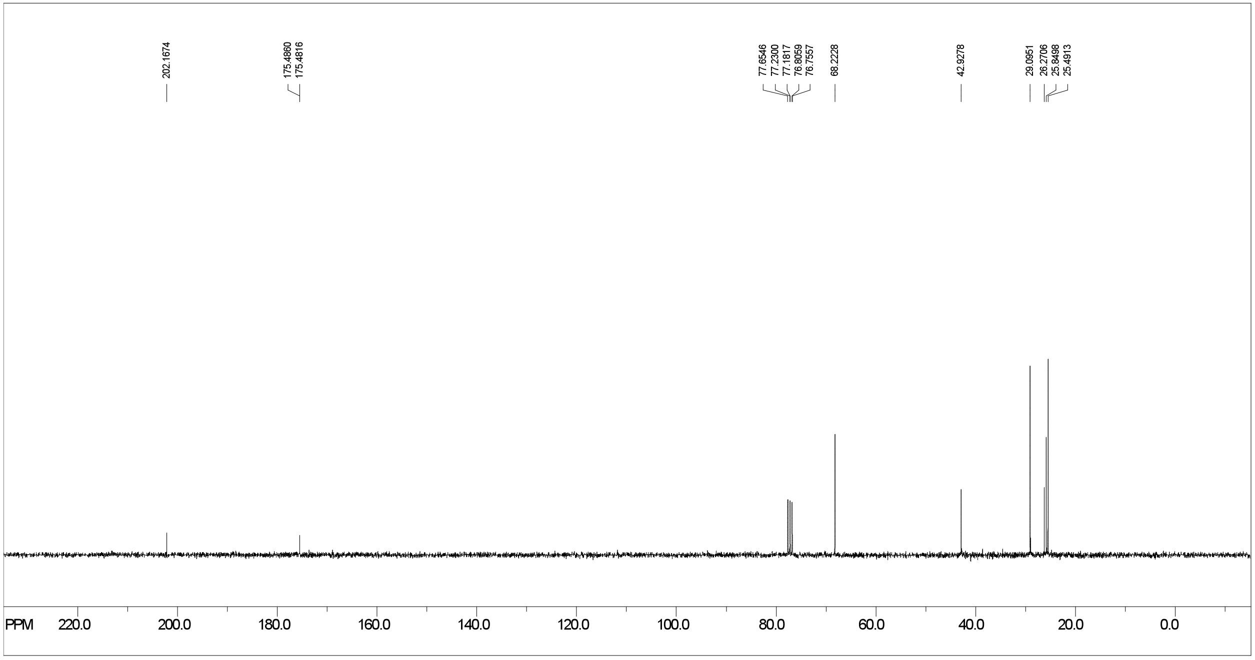
SpinWorks 2.5: STANDARD 1H OBSERVE



file: E:\ruili051509-H1.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 300.133009 MHz
time domain size: 19192 points
width: 4803.07 Hz = 16.003151 ppm = 0.250264 Hz/pt
number of scans: 8

freq. of 0 ppm: 300.131208 MHz
processed size: 32768 complex points
LB: 0.500 GB: 0.0000

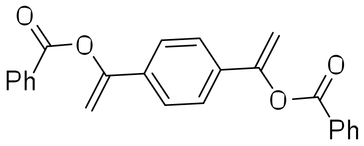
SpinWorks 2.5: 13C OBSERVE



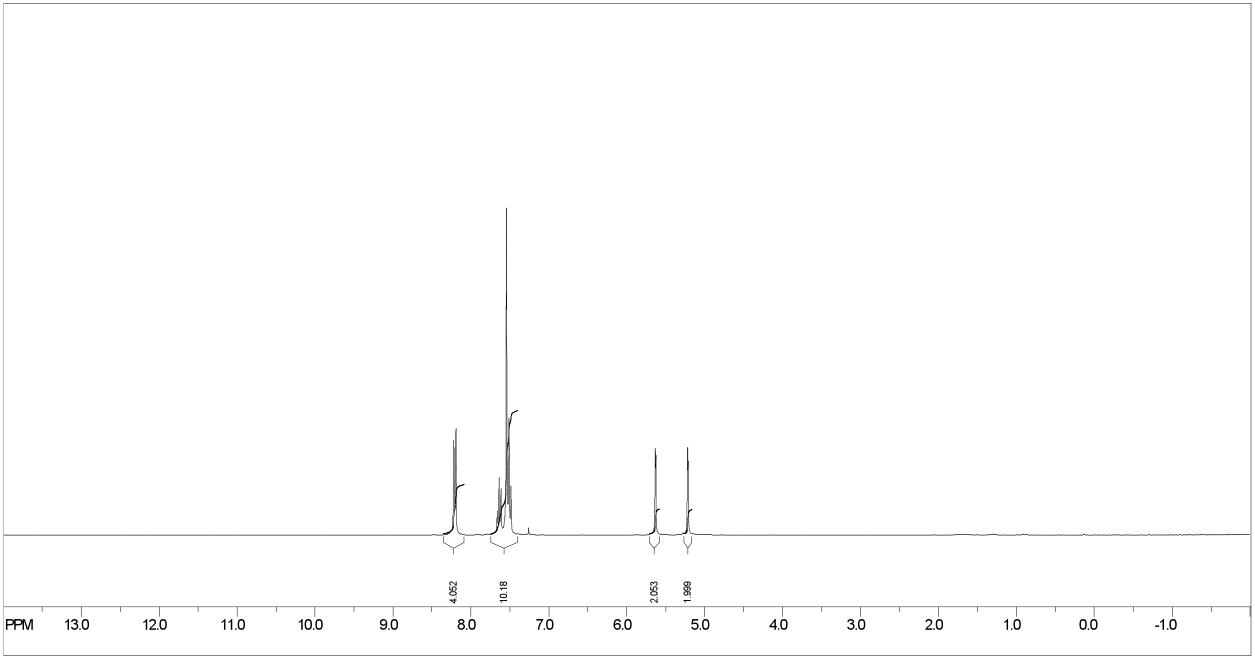
file: E:\ruili051509C.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 75.476336 MHz
time domain size: 68492 points
width: 18867.92 Hz = 249.984639 ppm = 0.275476 Hz/pt
number of scans: 256

freq. of 0 ppm: 75.468037 MHz
processed size: 131072 complex points
LB: 0.500 GB: 0.0000

5a



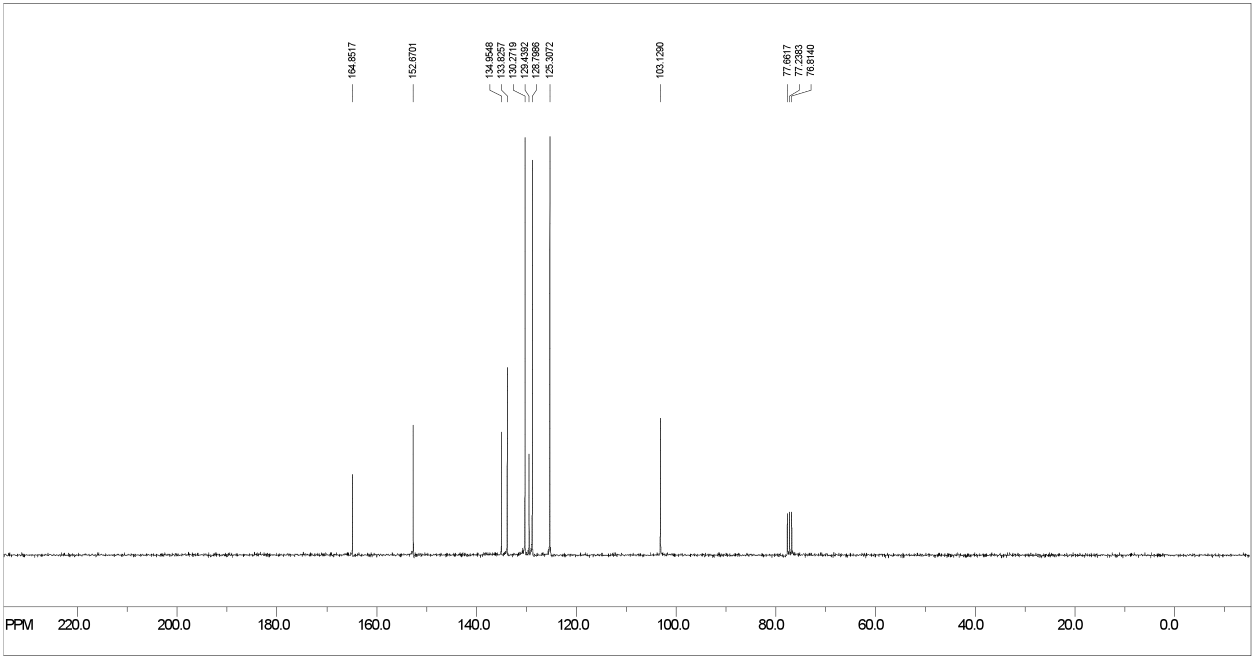
SpinWorks 2.5: STANDARD 1H OBSERVE



file: E:\ruili060209-H.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 300.133009 MHz
time domain size: 19192 points
width: 4803.07 Hz = 16.003151 ppm = 0.250264 Hz/pt
number of scans: 8

freq. of 0 ppm: 300.131208 MHz
processed size: 32768 complex points
LB: 0.500 GB: 0.0000

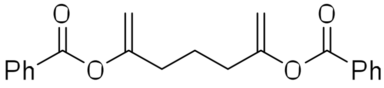
SpinWorks 2.5: 13C OBSERVE



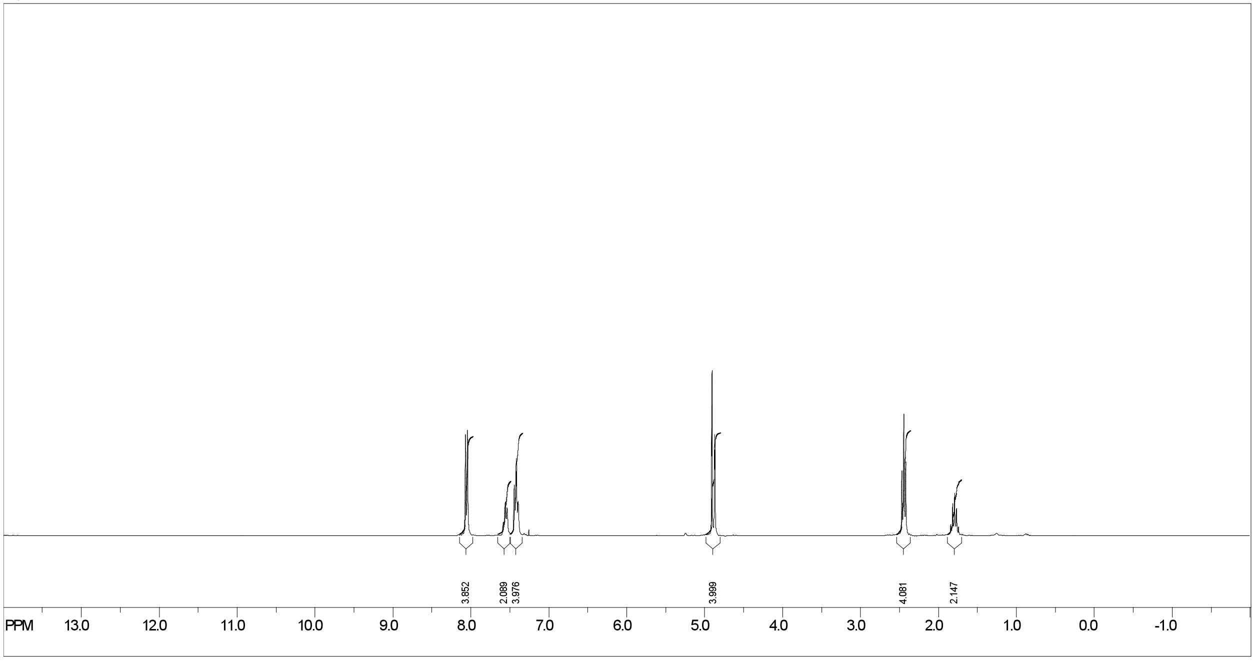
file: E:\ruili060209-C.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 75.476336 MHz
time domain size: 68492 points
width: 18867.92 Hz = 249.984639 ppm = 0.275476 Hz/pt
number of scans: 512

freq. of 0 ppm: 75.468044 MHz
processed size: 131072 complex points
LB: 0.500 GB: 0.0000

5b



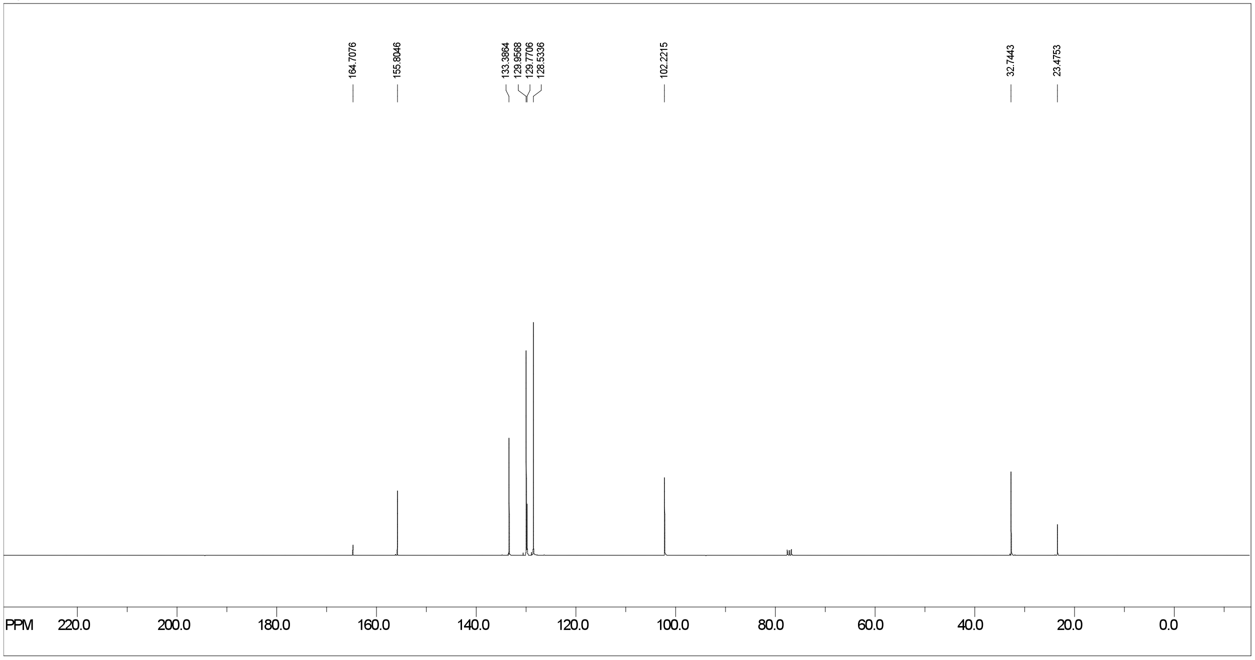
SpinWorks 2.5: STANDARD 1H OBSERVE



file: E:\ruili052709-H.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 300.133009 MHz
time domain size: 19192 points
width: 4803.07 Hz = 16.003151 ppm = 0.250264 Hz/pt
number of scans: 8

freq. of 0 ppm: 300.131208 MHz
processed size: 32768 complex points
LB: 0.500 GB: 0.0000

SpinWorks 2.5: 13C OBSERVE



file: E:\ruili052709-C.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 75.476336 MHz
time domain size: 68492 points
width: 18867.92 Hz = 249.984639 ppm = 0.275476 Hz/pt
number of scans: 640

freq. of 0 ppm: 75.468048 MHz
processed size: 131072 complex points
LB: 0.500 GB: 0.0000

Table S1. Crystal data and structure refinement for **6**.

Identification code	yi1ka	
Empirical formula	C45 H73 Cl O4 P2 Ru	
Formula weight	876.49	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	A b m 2	
Unit cell dimensions	a = 9.7750(2) Å	a= 90°.
	b = 24.8661(4) Å	b= 90°.
	c = 17.6805(3) Å	g = 90°.
Volume	4297.53(13) Å^3	
Z	4	
Density (calculated)	1.355 Mg/m^3	
Absorption coefficient	4.543 mm^{-1}	
F(000)	1864	
Crystal size	0.12 x 0.09 x 0.04 mm^3	
Theta range for data collection	3.55 to 67.20°.	
Index ranges	-11<=h<=0, -22<=k<=27, -17<=l<=21	
Reflections collected	10054	
Independent reflections	3201 [R(int) = 0.0231]	
Completeness to theta = 67.20°	98.2 %	
Absorption correction	Numerical	
Max. and min. transmission	0.8392 and 0.6117	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3201 / 1 / 263	
Goodness-of-fit on F^2	1.015	
Final R indices [I>2sigma(I)]	R1 = 0.0323, wR2 = 0.0793	
R indices (all data)	R1 = 0.0349, wR2 = 0.0808	
Absolute structure parameter	0.450(8)	
Largest diff. peak and hole	0.827 and -0.422 e.Å^{-3}	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **6**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1)	-413(1)	2500	1054(1)	19(1)
Cl(1)	-116(2)	2500	-279(1)	31(1)
P(1)	-452(1)	1525(1)	1100(1)	19(1)
O(1)	344(3)	2500	2201(2)	23(1)
O(2)	1769(3)	2500	1242(2)	24(1)
O(3)	6118(4)	2500	3899(2)	33(1)
O(10)	-3420(3)	2500	995(3)	30(1)
C(1)	2743(5)	2500	2480(3)	22(1)
C(2)	4075(7)	2500	2212(4)	26(1)
C(3)	5181(6)	2500	2689(3)	30(1)
C(4)	4957(9)	2500	3460(4)	22(1)
C(5)	3650(6)	2500	3753(4)	26(1)
C(6)	2545(5)	2500	3249(3)	24(1)
C(7)	1583(5)	2500	1949(3)	23(1)
C(8)	5939(8)	2500	4690(4)	38(2)
C(10)	-2327(6)	2500	1043(5)	27(1)
C(11)	-1358(4)	1215(2)	1934(2)	24(1)
C(12)	-2890(4)	1319(2)	1955(2)	31(1)
C(13)	-3563(4)	1015(2)	2618(3)	37(1)
C(14)	-2918(5)	1144(2)	3365(3)	36(1)
C(15)	-1356(4)	1065(2)	3332(3)	41(1)
C(16)	-732(4)	1393(2)	2688(2)	36(1)
C(21)	-1164(4)	1190(2)	254(2)	22(1)
C(22)	-2461(4)	1447(2)	-73(2)	26(1)
C(23)	-2879(4)	1187(2)	-840(3)	30(1)
C(24)	-3051(4)	580(2)	-757(2)	32(1)
C(25)	-1749(4)	327(2)	-444(2)	32(1)
C(26)	-1347(4)	583(2)	316(2)	29(1)
C(31)	1310(3)	1249(2)	1222(2)	26(1)
C(32)	2148(3)	1311(2)	490(3)	28(1)
C(33)	3665(4)	1196(2)	643(2)	34(1)

C(34)	3880(3)	652(2)	997(4)	38(1)
C(35)	3020(4)	586(2)	1707(3)	42(1)
C(36)	1506(4)	681(2)	1555(3)	37(1)

Table S3. Bond lengths [Å] and angles [°] for **6**.

Ru(1)-C(10)	1.871(5)
Ru(1)-O(2)	2.159(3)
Ru(1)-O(1)	2.159(4)
Ru(1)-Cl(1)	2.3755(16)
Ru(1)-P(1)	2.4267(8)
Ru(1)-P(1)#1	2.4267(8)
Ru(1)-C(7)	2.512(6)
P(1)-C(21)	1.847(4)
P(1)-C(31)	1.867(4)
P(1)-C(11)	1.885(4)
O(1)-C(7)	1.290(6)
O(2)-C(7)	1.264(7)
O(3)-C(4)	1.374(9)
O(3)-C(8)	1.410(8)
O(10)-C(10)	1.073(6)
C(1)-C(6)	1.374(8)
C(1)-C(2)	1.386(8)
C(1)-C(7)	1.472(7)
C(2)-C(3)	1.372(9)
C(2)-H(2)	0.9500
C(3)-C(4)	1.381(10)
C(3)-H(3)	0.9500
C(4)-C(5)	1.379(11)
C(5)-C(6)	1.400(8)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(11)-C(12)	1.521(5)
C(11)-C(16)	1.533(6)
C(11)-H(11)	1.0000
C(12)-C(13)	1.543(6)
C(12)-H(12A)	0.9900

C(12)-H(12B)	0.9900
C(13)-C(14)	1.498(6)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-C(15)	1.541(6)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-C(16)	1.529(6)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(21)-C(26)	1.525(5)
C(21)-C(22)	1.533(5)
C(21)-H(21)	1.0000
C(22)-C(23)	1.557(6)
C(22)-H(22A)	0.9900
C(22)-H(22B)	0.9900
C(23)-C(24)	1.526(6)
C(23)-H(23A)	0.9900
C(23)-H(23B)	0.9900
C(24)-C(25)	1.524(5)
C(24)-H(24A)	0.9900
C(24)-H(24B)	0.9900
C(25)-C(26)	1.538(6)
C(25)-H(25A)	0.9900
C(25)-H(25B)	0.9900
C(26)-H(26A)	0.9900
C(26)-H(26B)	0.9900
C(31)-C(32)	1.539(6)
C(31)-C(36)	1.542(6)
C(31)-H(31)	1.0000
C(32)-C(33)	1.534(5)
C(32)-H(32A)	0.9900
C(32)-H(32B)	0.9900
C(33)-C(34)	1.505(6)

C(33)-H(33A)	0.9900
C(33)-H(33B)	0.9900
C(34)-C(35)	1.520(7)
C(34)-H(34A)	0.9900
C(34)-H(34B)	0.9900
C(35)-C(36)	1.522(5)
C(35)-H(35A)	0.9900
C(35)-H(35B)	0.9900
C(36)-H(36A)	0.9900
C(36)-H(36B)	0.9900
C(10)-Ru(1)-O(2)	171.7(3)
C(10)-Ru(1)-O(1)	110.6(3)
O(2)-Ru(1)-O(1)	61.11(13)
C(10)-Ru(1)-Cl(1)	96.4(3)
O(2)-Ru(1)-Cl(1)	91.84(10)
O(1)-Ru(1)-Cl(1)	152.95(11)
C(10)-Ru(1)-P(1)	89.13(2)
O(2)-Ru(1)-P(1)	90.588(19)
O(1)-Ru(1)-P(1)	88.52(3)
Cl(1)-Ru(1)-P(1)	91.99(3)
C(10)-Ru(1)-P(1)#1	89.13(2)
O(2)-Ru(1)-P(1)#1	90.588(19)
O(1)-Ru(1)-P(1)#1	88.52(3)
Cl(1)-Ru(1)-P(1)#1	91.99(3)
P(1)-Ru(1)-P(1)#1	175.81(6)
C(10)-Ru(1)-C(7)	141.5(3)
O(2)-Ru(1)-C(7)	30.21(15)
O(1)-Ru(1)-C(7)	30.90(16)
Cl(1)-Ru(1)-C(7)	122.05(14)
P(1)-Ru(1)-C(7)	89.50(3)
P(1)#1-Ru(1)-C(7)	89.50(3)
C(21)-P(1)-C(31)	106.02(17)
C(21)-P(1)-C(11)	105.77(15)
C(31)-P(1)-C(11)	101.11(18)
C(21)-P(1)-Ru(1)	115.40(14)

C(31)-P(1)-Ru(1)	110.92(12)
C(11)-P(1)-Ru(1)	116.22(15)
C(7)-O(1)-Ru(1)	89.9(3)
C(7)-O(2)-Ru(1)	90.6(3)
C(4)-O(3)-C(8)	117.2(6)
C(6)-C(1)-C(2)	118.1(5)
C(6)-C(1)-C(7)	121.5(5)
C(2)-C(1)-C(7)	120.4(5)
C(3)-C(2)-C(1)	122.0(6)
C(3)-C(2)-H(2)	119.0
C(1)-C(2)-H(2)	119.0
C(2)-C(3)-C(4)	118.8(6)
C(2)-C(3)-H(3)	120.6
C(4)-C(3)-H(3)	120.6
O(3)-C(4)-C(5)	123.6(6)
O(3)-C(4)-C(3)	115.2(7)
C(5)-C(4)-C(3)	121.2(7)
C(4)-C(5)-C(6)	118.4(6)
C(4)-C(5)-H(5)	120.8
C(6)-C(5)-H(5)	120.8
C(1)-C(6)-C(5)	121.4(5)
C(1)-C(6)-H(6)	119.3
C(5)-C(6)-H(6)	119.3
O(2)-C(7)-O(1)	118.5(5)
O(2)-C(7)-C(1)	121.3(5)
O(1)-C(7)-C(1)	120.2(5)
O(2)-C(7)-Ru(1)	59.2(3)
O(1)-C(7)-Ru(1)	59.2(3)
C(1)-C(7)-Ru(1)	179.4(4)
O(3)-C(8)-H(8A)	109.5
O(3)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
O(3)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
O(10)-C(10)-Ru(1)	176.0(7)

C(12)-C(11)-C(16)	108.8(4)
C(12)-C(11)-P(1)	114.4(3)
C(16)-C(11)-P(1)	112.0(3)
C(12)-C(11)-H(11)	107.1
C(16)-C(11)-H(11)	107.1
P(1)-C(11)-H(11)	107.1
C(11)-C(12)-C(13)	110.8(3)
C(11)-C(12)-H(12A)	109.5
C(13)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
C(13)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	108.1
C(14)-C(13)-C(12)	112.7(4)
C(14)-C(13)-H(13A)	109.1
C(12)-C(13)-H(13A)	109.1
C(14)-C(13)-H(13B)	109.1
C(12)-C(13)-H(13B)	109.1
H(13A)-C(13)-H(13B)	107.8
C(13)-C(14)-C(15)	110.9(4)
C(13)-C(14)-H(14A)	109.5
C(15)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
C(15)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	108.1
C(16)-C(15)-C(14)	110.7(4)
C(16)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15A)	109.5
C(16)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	108.1
C(15)-C(16)-C(11)	109.5(4)
C(15)-C(16)-H(16A)	109.8
C(11)-C(16)-H(16A)	109.8
C(15)-C(16)-H(16B)	109.8
C(11)-C(16)-H(16B)	109.8
H(16A)-C(16)-H(16B)	108.2

C(26)-C(21)-C(22)	110.1(3)
C(26)-C(21)-P(1)	115.6(3)
C(22)-C(21)-P(1)	115.4(3)
C(26)-C(21)-H(21)	104.8
C(22)-C(21)-H(21)	104.8
P(1)-C(21)-H(21)	104.8
C(21)-C(22)-C(23)	111.8(3)
C(21)-C(22)-H(22A)	109.3
C(23)-C(22)-H(22A)	109.3
C(21)-C(22)-H(22B)	109.3
C(23)-C(22)-H(22B)	109.3
H(22A)-C(22)-H(22B)	107.9
C(24)-C(23)-C(22)	110.9(4)
C(24)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23A)	109.5
C(24)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	108.0
C(25)-C(24)-C(23)	110.5(3)
C(25)-C(24)-H(24A)	109.6
C(23)-C(24)-H(24A)	109.6
C(25)-C(24)-H(24B)	109.6
C(23)-C(24)-H(24B)	109.6
H(24A)-C(24)-H(24B)	108.1
C(24)-C(25)-C(26)	111.2(3)
C(24)-C(25)-H(25A)	109.4
C(26)-C(25)-H(25A)	109.4
C(24)-C(25)-H(25B)	109.4
C(26)-C(25)-H(25B)	109.4
H(25A)-C(25)-H(25B)	108.0
C(21)-C(26)-C(25)	112.1(3)
C(21)-C(26)-H(26A)	109.2
C(25)-C(26)-H(26A)	109.2
C(21)-C(26)-H(26B)	109.2
C(25)-C(26)-H(26B)	109.2
H(26A)-C(26)-H(26B)	107.9

C(32)-C(31)-C(36)	110.3(3)
C(32)-C(31)-P(1)	110.9(3)
C(36)-C(31)-P(1)	119.7(3)
C(32)-C(31)-H(31)	104.8
C(36)-C(31)-H(31)	104.8
P(1)-C(31)-H(31)	104.8
C(33)-C(32)-C(31)	110.3(3)
C(33)-C(32)-H(32A)	109.6
C(31)-C(32)-H(32A)	109.6
C(33)-C(32)-H(32B)	109.6
C(31)-C(32)-H(32B)	109.6
H(32A)-C(32)-H(32B)	108.1
C(34)-C(33)-C(32)	112.0(3)
C(34)-C(33)-H(33A)	109.2
C(32)-C(33)-H(33A)	109.2
C(34)-C(33)-H(33B)	109.2
C(32)-C(33)-H(33B)	109.2
H(33A)-C(33)-H(33B)	107.9
C(33)-C(34)-C(35)	111.3(3)
C(33)-C(34)-H(34A)	109.4
C(35)-C(34)-H(34A)	109.4
C(33)-C(34)-H(34B)	109.4
C(35)-C(34)-H(34B)	109.4
H(34A)-C(34)-H(34B)	108.0
C(34)-C(35)-C(36)	112.1(4)
C(34)-C(35)-H(35A)	109.2
C(36)-C(35)-H(35A)	109.2
C(34)-C(35)-H(35B)	109.2
C(36)-C(35)-H(35B)	109.2
H(35A)-C(35)-H(35B)	107.9
C(35)-C(36)-C(31)	109.2(3)
C(35)-C(36)-H(36A)	109.8
C(31)-C(36)-H(36A)	109.8
C(35)-C(36)-H(36B)	109.8
C(31)-C(36)-H(36B)	109.8
H(36A)-C(36)-H(36B)	108.3

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+1/2,z+0

Table S4. Anisotropic displacement parameters (Å^{2}x 10^3) for **6**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	16(1)	22(1)	18(1)	0	-2(1)	0
Cl(1)	30(1)	35(1)	28(1)	0	-2(1)	0
P(1)	17(1)	21(1)	20(1)	0(1)	-2(1)	0(1)
O(1)	26(3)	27(2)	15(2)	0	-7(2)	0
O(2)	19(2)	28(2)	25(3)	0	-1(1)	0
O(3)	30(2)	37(2)	33(3)	0	-5(2)	0
O(10)	26(2)	29(2)	35(2)	0	0(3)	0
C(1)	23(3)	18(3)	24(3)	0	-1(2)	0
C(2)	28(3)	29(3)	23(3)	0	-2(3)	0
C(3)	21(3)	38(3)	32(4)	0	4(3)	0
C(4)	23(2)	20(2)	23(4)	0	-8(2)	0
C(5)	35(3)	23(3)	21(3)	0	0(3)	0
C(6)	21(3)	22(3)	27(3)	0	5(2)	0
C(7)	24(3)	19(3)	26(4)	0	4(2)	0
C(8)	45(4)	33(4)	37(5)	0	-17(3)	0
C(10)	47(3)	17(2)	17(3)	0	-9(4)	0
C(11)	28(2)	29(2)	14(2)	3(2)	3(2)	-3(2)
C(12)	25(2)	46(3)	22(2)	6(2)	-1(2)	6(2)
C(13)	24(2)	53(3)	33(3)	7(2)	2(2)	-1(2)
C(14)	47(3)	44(3)	18(2)	4(2)	8(2)	0(2)
C(15)	41(2)	61(3)	23(2)	11(2)	-10(2)	-9(2)
C(16)	32(2)	52(3)	26(3)	2(2)	0(2)	-10(2)
C(21)	17(2)	25(2)	24(3)	-1(2)	2(2)	-1(2)
C(22)	23(2)	33(2)	23(2)	-4(2)	-4(2)	-3(2)
C(23)	27(2)	33(2)	30(3)	-1(2)	-5(2)	-2(2)
C(24)	32(2)	37(2)	28(3)	-8(2)	-5(2)	-6(2)
C(25)	38(2)	24(2)	33(2)	-3(2)	-2(2)	1(2)
C(26)	30(2)	28(2)	30(2)	1(2)	-6(2)	1(2)
C(31)	19(2)	28(2)	30(3)	-1(2)	-5(2)	0(1)
C(32)	20(2)	33(2)	32(2)	-5(2)	0(2)	4(2)
C(33)	19(2)	46(3)	36(3)	-7(2)	-2(2)	1(2)

C(34)	20(2)	34(2)	61(3)	-10(3)	-10(3)	5(1)
C(35)	33(2)	31(3)	63(4)	8(2)	-10(2)	8(2)
C(36)	26(2)	30(2)	55(3)	4(2)	-4(2)	3(2)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **6**.

	x	y	z	U(eq)
H(2)	4226	2500	1681	32
H(3)	6085	2500	2493	36
H(5)	3502	2500	4284	31
H(6)	1639	2500	3444	28
H(8A)	6835	2500	4938	57
H(8B)	5428	2178	4841	57
H(8C)	5428	2822	4841	57
H(11)	-1229	817	1896	28
H(12A)	-3307	1201	1473	37
H(12B)	-3059	1710	2011	37
H(13A)	-4547	1108	2638	44
H(13B)	-3490	623	2526	44
H(14A)	-3310	909	3761	44
H(14B)	-3125	1522	3501	44
H(15A)	-945	1177	3819	50
H(15B)	-1148	679	3255	50
H(16A)	271	1340	2677	44
H(16B)	-915	1780	2771	44
H(21)	-454	1240	-147	26
H(22A)	-2303	1837	-149	32
H(22B)	-3220	1406	293	32
H(23A)	-3749	1347	-1017	36
H(23B)	-2167	1263	-1224	36
H(24A)	-3825	503	-412	39
H(24B)	-3265	420	-1256	39
H(25A)	-996	377	-811	38
H(25B)	-1892	-64	-374	38
H(26A)	-2064	504	695	35
H(26B)	-481	420	495	35
H(31)	1760	1495	1593	31
H(32A)	1802	1057	103	34
H(32B)	2043	1681	291	34

H(33A)	4179	1215	161	40
H(33B)	4034	1477	984	40
H(34A)	4859	608	1126	46
H(34B)	3632	369	628	46
H(35A)	3339	844	2095	51
H(35B)	3148	219	1910	51
H(36A)	983	647	2032	45
H(36B)	1160	408	1195	45

Table S6. Torsion angles [°] for **6**.

C(10)-Ru(1)-P(1)-C(21)	65.2(3)
O(2)-Ru(1)-P(1)-C(21)	-123.07(17)
O(1)-Ru(1)-P(1)-C(21)	175.86(17)
Cl(1)-Ru(1)-P(1)-C(21)	-31.20(15)
P(1)#1-Ru(1)-P(1)-C(21)	130.7(6)
C(7)-Ru(1)-P(1)-C(21)	-153.3(2)
C(10)-Ru(1)-P(1)-C(31)	-174.2(3)
O(2)-Ru(1)-P(1)-C(31)	-2.49(17)
O(1)-Ru(1)-P(1)-C(31)	-63.57(16)
Cl(1)-Ru(1)-P(1)-C(31)	89.37(14)
P(1)#1-Ru(1)-P(1)-C(31)	-108.8(6)
C(7)-Ru(1)-P(1)-C(31)	-32.68(19)
C(10)-Ru(1)-P(1)-C(11)	-59.5(3)
O(2)-Ru(1)-P(1)-C(11)	112.23(18)
O(1)-Ru(1)-P(1)-C(11)	51.16(17)
Cl(1)-Ru(1)-P(1)-C(11)	-155.90(16)
P(1)#1-Ru(1)-P(1)-C(11)	6.0(7)
C(7)-Ru(1)-P(1)-C(11)	82.0(2)
C(10)-Ru(1)-O(1)-C(7)	180.0
O(2)-Ru(1)-O(1)-C(7)	0.0
Cl(1)-Ru(1)-O(1)-C(7)	0.0
P(1)-Ru(1)-O(1)-C(7)	91.49(2)
P(1)#1-Ru(1)-O(1)-C(7)	-91.49(2)
C(10)-Ru(1)-O(2)-C(7)	0.0
O(1)-Ru(1)-O(2)-C(7)	0.0
Cl(1)-Ru(1)-O(2)-C(7)	180.0
P(1)-Ru(1)-O(2)-C(7)	-87.99(3)
P(1)#1-Ru(1)-O(2)-C(7)	87.99(3)
C(6)-C(1)-C(2)-C(3)	0.0
C(7)-C(1)-C(2)-C(3)	180.0
C(1)-C(2)-C(3)-C(4)	0.000(1)
C(8)-O(3)-C(4)-C(5)	0.000(1)
C(8)-O(3)-C(4)-C(3)	180.0
C(2)-C(3)-C(4)-O(3)	180.0

C(2)-C(3)-C(4)-C(5)	0.000(1)
O(3)-C(4)-C(5)-C(6)	180.000(1)
C(3)-C(4)-C(5)-C(6)	0.000(1)
C(2)-C(1)-C(6)-C(5)	0.0
C(7)-C(1)-C(6)-C(5)	180.0
C(4)-C(5)-C(6)-C(1)	0.000(1)
Ru(1)-O(2)-C(7)-O(1)	0.0
Ru(1)-O(2)-C(7)-C(1)	180.0
Ru(1)-O(1)-C(7)-O(2)	0.0
Ru(1)-O(1)-C(7)-C(1)	180.0
C(6)-C(1)-C(7)-O(2)	180.0
C(2)-C(1)-C(7)-O(2)	0.0
C(6)-C(1)-C(7)-O(1)	0.0
C(2)-C(1)-C(7)-O(1)	180.0
C(6)-C(1)-C(7)-Ru(1)	0.00(5)
C(2)-C(1)-C(7)-Ru(1)	180.00(5)
C(10)-Ru(1)-C(7)-O(2)	180.0
O(1)-Ru(1)-C(7)-O(2)	180.0
Cl(1)-Ru(1)-C(7)-O(2)	0.0
P(1)-Ru(1)-C(7)-O(2)	92.04(3)
P(1)#1-Ru(1)-C(7)-O(2)	-92.04(3)
C(10)-Ru(1)-C(7)-O(1)	0.0
O(2)-Ru(1)-C(7)-O(1)	180.0
Cl(1)-Ru(1)-C(7)-O(1)	180.0
P(1)-Ru(1)-C(7)-O(1)	-87.96(3)
P(1)#1-Ru(1)-C(7)-O(1)	87.96(3)
C(10)-Ru(1)-C(7)-C(1)	0.00(4)
O(2)-Ru(1)-C(7)-C(1)	180.00(4)
O(1)-Ru(1)-C(7)-C(1)	0.00(4)
Cl(1)-Ru(1)-C(7)-C(1)	180.00(4)
P(1)-Ru(1)-C(7)-C(1)	-87.97(5)
P(1)#1-Ru(1)-C(7)-C(1)	87.96(5)
O(2)-Ru(1)-C(10)-O(10)	180.000(2)
O(1)-Ru(1)-C(10)-O(10)	180.000(3)
Cl(1)-Ru(1)-C(10)-O(10)	0.000(3)
P(1)-Ru(1)-C(10)-O(10)	-91.91(3)

P(1)#1-Ru(1)-C(10)-O(10)	91.91(4)
C(7)-Ru(1)-C(10)-O(10)	180.000(3)
C(21)-P(1)-C(11)-C(12)	-63.8(3)
C(31)-P(1)-C(11)-C(12)	-174.2(3)
Ru(1)-P(1)-C(11)-C(12)	65.7(3)
C(21)-P(1)-C(11)-C(16)	171.8(3)
C(31)-P(1)-C(11)-C(16)	61.5(3)
Ru(1)-P(1)-C(11)-C(16)	-58.7(3)
C(16)-C(11)-C(12)-C(13)	-58.4(5)
P(1)-C(11)-C(12)-C(13)	175.5(3)
C(11)-C(12)-C(13)-C(14)	55.2(5)
C(12)-C(13)-C(14)-C(15)	-52.5(5)
C(13)-C(14)-C(15)-C(16)	55.1(5)
C(14)-C(15)-C(16)-C(11)	-59.8(5)
C(12)-C(11)-C(16)-C(15)	61.3(5)
P(1)-C(11)-C(16)-C(15)	-171.2(3)
C(31)-P(1)-C(21)-C(26)	63.7(3)
C(11)-P(1)-C(21)-C(26)	-43.1(3)
Ru(1)-P(1)-C(21)-C(26)	-173.1(2)
C(31)-P(1)-C(21)-C(22)	-165.8(3)
C(11)-P(1)-C(21)-C(22)	87.4(3)
Ru(1)-P(1)-C(21)-C(22)	-42.6(3)
C(26)-C(21)-C(22)-C(23)	-54.4(5)
P(1)-C(21)-C(22)-C(23)	172.5(3)
C(21)-C(22)-C(23)-C(24)	55.6(4)
C(22)-C(23)-C(24)-C(25)	-56.0(4)
C(23)-C(24)-C(25)-C(26)	56.7(5)
C(22)-C(21)-C(26)-C(25)	55.1(4)
P(1)-C(21)-C(26)-C(25)	-171.9(3)
C(24)-C(25)-C(26)-C(21)	-56.8(4)
C(21)-P(1)-C(31)-C(32)	53.6(3)
C(11)-P(1)-C(31)-C(32)	163.7(3)
Ru(1)-P(1)-C(31)-C(32)	-72.4(3)
C(21)-P(1)-C(31)-C(36)	-76.7(4)
C(11)-P(1)-C(31)-C(36)	33.5(4)
Ru(1)-P(1)-C(31)-C(36)	157.4(3)

C(36)-C(31)-C(32)-C(33)	-57.1(4)
P(1)-C(31)-C(32)-C(33)	167.9(3)
C(31)-C(32)-C(33)-C(34)	55.3(5)
C(32)-C(33)-C(34)-C(35)	-54.2(5)
C(33)-C(34)-C(35)-C(36)	55.9(5)
C(34)-C(35)-C(36)-C(31)	-57.5(5)
C(32)-C(31)-C(36)-C(35)	58.1(5)
P(1)-C(31)-C(36)-C(35)	-171.4(3)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+1/2,z+0

Table S7. Crystal data and structure refinement for **7**.

Identification code	yi1na	
Empirical formula	C59 H93 Cl O4 P2 Ru	
Formula weight	1064.79	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.9925(2) Å	a= 103.0180(10)°.
	b = 12.9129(2) Å	b= 98.7440(10)°.
	c = 21.9786(5) Å	g = 107.5620(10)°.
Volume	2815.46(9) Å^3	
Z	2	
Density (calculated)	1.256 Mg/m^3	
Absorption coefficient	3.558 mm^{-1}	
F(000)	1140	
Crystal size	0.40 x 0.23 x 0.17 mm^3	
Theta range for data collection	3.74 to 67.81°.	
Index ranges	-13<=h<=12, -15<=k<=15, 0<=l<=26	
Reflections collected	23248	
Independent reflections	9565 [R(int) = 0.0242]	
Completeness to theta = 67.81°	93.5 %	
Absorption correction	Numerical	
Max. and min. transmission	0.5897 and 0.3317	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9565 / 0 / 607	
Goodness-of-fit on F^2	1.012	
Final R indices [I>2sigma(I)]	R1 = 0.0295, wR2 = 0.0722	
R indices (all data)	R1 = 0.0321, wR2 = 0.0735	
Largest diff. peak and hole	0.514 and -0.363 e.Å^{-3}	

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **7**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1)	8688(1)	1834(1)	7813(1)	16(1)
Cl(1)	9936(1)	1389(1)	6997(1)	21(1)
P(1)	9317(1)	3721(1)	7673(1)	17(1)
P(2)	8229(1)	-91(1)	7874(1)	18(1)
O(1)	7033(1)	1281(1)	7026(1)	20(1)
O(2)	6040(1)	1784(1)	7797(1)	21(1)
O(3)	1394(2)	86(2)	5313(1)	41(1)
O(10)	10657(2)	2709(1)	9068(1)	25(1)
C(10)	9930(2)	2364(2)	8571(1)	21(1)
C(11)	11061(2)	4263(2)	7604(1)	19(1)
C(12)	12038(2)	3890(2)	8006(1)	22(1)
C(13)	13332(2)	4164(2)	7788(1)	26(1)
C(14)	13940(2)	5414(2)	7843(1)	28(1)
C(15)	12961(2)	5839(2)	7498(1)	27(1)
C(16)	11668(2)	5545(2)	7715(1)	24(1)
C(21)	9129(2)	4892(2)	8279(1)	19(1)
C(22)	9853(2)	5047(2)	8966(1)	23(1)
C(23)	9780(2)	6093(2)	9431(1)	26(1)
C(24)	8359(2)	6022(2)	9407(1)	30(1)
C(25)	7617(2)	5841(2)	8722(1)	26(1)
C(26)	7686(2)	4794(2)	8253(1)	23(1)
C(31)	8321(2)	3790(2)	6921(1)	21(1)
C(32)	8543(2)	4974(2)	6833(1)	28(1)
C(33)	7494(3)	4931(2)	6277(1)	36(1)
C(34)	7500(3)	4126(2)	5654(1)	37(1)
C(35)	7340(2)	2955(2)	5729(1)	31(1)
C(36)	8376(2)	2996(2)	6298(1)	24(1)
C(41)	7598(2)	-489(2)	8561(1)	22(1)
C(42)	6175(2)	-553(2)	8545(1)	26(1)
C(43)	5714(2)	-1020(2)	9087(1)	32(1)
C(44)	6621(2)	-303(2)	9743(1)	36(1)

C(45)	8040(2)	-200(2)	9757(1)	33(1)
C(46)	8505(2)	260(2)	9214(1)	25(1)
C(51)	6930(2)	-1148(2)	7168(1)	21(1)
C(52)	6460(2)	-2390(2)	7181(1)	26(1)
C(53)	5236(2)	-3103(2)	6635(1)	31(1)
C(54)	5505(2)	-3044(2)	5983(1)	29(1)
C(55)	6039(2)	-1825(2)	5965(1)	27(1)
C(56)	7254(2)	-1114(2)	6513(1)	23(1)
C(61)	9686(2)	-558(2)	7873(1)	21(1)
C(62)	11031(2)	382(2)	8201(1)	24(1)
C(63)	12138(2)	-59(2)	8062(1)	28(1)
C(64)	12066(2)	-1101(2)	8287(1)	31(1)
C(65)	10724(2)	-2020(2)	8001(1)	30(1)
C(66)	9610(2)	-1581(2)	8128(1)	25(1)
C(70)	6041(2)	1379(2)	7188(1)	20(1)
C(71)	4814(2)	1062(2)	6707(1)	20(1)
C(72)	3670(2)	1180(2)	6859(1)	26(1)
C(73)	2547(2)	848(2)	6384(1)	30(1)
C(74)	2545(2)	388(2)	5744(1)	26(1)
C(75)	3682(2)	273(2)	5584(1)	23(1)
C(76)	4801(2)	611(2)	6067(1)	23(1)
C(77)	1333(2)	-373(2)	4649(1)	36(1)
C(80)	7229(2)	2459(2)	8875(1)	21(1)
C(81)	6223(2)	2716(2)	9187(1)	22(1)
C(82)	5009(2)	2697(2)	8874(1)	28(1)
C(83)	4144(2)	3004(2)	9217(1)	34(1)
C(84)	4481(3)	3352(2)	9878(1)	38(1)
C(85)	5683(3)	3367(3)	10198(1)	48(1)
C(86)	6519(2)	3047(2)	9857(1)	38(1)
C(90)	7291(2)	2079(2)	8267(1)	20(1)
C(1S)	3502(3)	3539(2)	5819(1)	47(1)
C(2S)	2087(3)	3483(3)	5632(1)	50(1)
C(3S)	1465(3)	2961(2)	4918(1)	42(1)
C(4S)	101(3)	2977(3)	4699(1)	47(1)
C(5S)	-500(3)	2441(3)	3986(2)	53(1)
C(6S)	-1871(3)	2476(3)	3767(2)	65(1)

Table S9. Bond lengths [Å] and angles [°] for **7**.

Ru(1)-C(10)	1.827(2)
Ru(1)-C(90)	2.017(2)
Ru(1)-O(1)	2.1246(14)
Ru(1)-P(2)	2.4216(5)
Ru(1)-P(1)	2.4289(5)
Ru(1)-Cl(1)	2.4872(5)
P(1)-C(21)	1.862(2)
P(1)-C(11)	1.875(2)
P(1)-C(31)	1.875(2)
P(2)-C(41)	1.864(2)
P(2)-C(51)	1.872(2)
P(2)-C(61)	1.873(2)
O(1)-C(70)	1.231(2)
O(2)-C(70)	1.324(2)
O(2)-C(90)	1.476(2)
O(3)-C(74)	1.349(3)
O(3)-C(77)	1.429(3)
O(10)-C(10)	1.154(3)
C(11)-C(16)	1.532(3)
C(11)-C(12)	1.543(3)
C(11)-H(11A)	1.0000
C(12)-C(13)	1.535(3)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-C(14)	1.517(3)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-C(15)	1.527(3)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-C(16)	1.535(3)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-H(16A)	0.9900

C(16)-H(16B)	0.9900
C(21)-C(22)	1.535(3)
C(21)-C(26)	1.544(3)
C(21)-H(21A)	1.0000
C(22)-C(23)	1.531(3)
C(22)-H(22A)	0.9900
C(22)-H(22B)	0.9900
C(23)-C(24)	1.528(3)
C(23)-H(23A)	0.9900
C(23)-H(23B)	0.9900
C(24)-C(25)	1.529(3)
C(24)-H(24A)	0.9900
C(24)-H(24B)	0.9900
C(25)-C(26)	1.535(3)
C(25)-H(25A)	0.9900
C(25)-H(25B)	0.9900
C(26)-H(26A)	0.9900
C(26)-H(26B)	0.9900
C(31)-C(32)	1.535(3)
C(31)-C(36)	1.536(3)
C(31)-H(31A)	1.0000
C(32)-C(33)	1.527(3)
C(32)-H(32A)	0.9900
C(32)-H(32B)	0.9900
C(33)-C(34)	1.524(3)
C(33)-H(33A)	0.9900
C(33)-H(33B)	0.9900
C(34)-C(35)	1.518(4)
C(34)-H(34A)	0.9900
C(34)-H(34B)	0.9900
C(35)-C(36)	1.538(3)
C(35)-H(35A)	0.9900
C(35)-H(35B)	0.9900
C(36)-H(36A)	0.9900
C(36)-H(36B)	0.9900
C(41)-C(46)	1.532(3)

C(41)-C(42)	1.537(3)
C(41)-H(41A)	1.0000
C(42)-C(43)	1.537(3)
C(42)-H(42A)	0.9900
C(42)-H(42B)	0.9900
C(43)-C(44)	1.528(3)
C(43)-H(43A)	0.9900
C(43)-H(43B)	0.9900
C(44)-C(45)	1.520(3)
C(44)-H(44A)	0.9900
C(44)-H(44B)	0.9900
C(45)-C(46)	1.537(3)
C(45)-H(45A)	0.9900
C(45)-H(45B)	0.9900
C(46)-H(46A)	0.9900
C(46)-H(46B)	0.9900
C(51)-C(52)	1.537(3)
C(51)-C(56)	1.542(3)
C(51)-H(51A)	1.0000
C(52)-C(53)	1.536(3)
C(52)-H(52A)	0.9900
C(52)-H(52B)	0.9900
C(53)-C(54)	1.522(3)
C(53)-H(53A)	0.9900
C(53)-H(53B)	0.9900
C(54)-C(55)	1.517(3)
C(54)-H(54A)	0.9900
C(54)-H(54B)	0.9900
C(55)-C(56)	1.533(3)
C(55)-H(55A)	0.9900
C(55)-H(55B)	0.9900
C(56)-H(56A)	0.9900
C(56)-H(56B)	0.9900
C(61)-C(66)	1.533(3)
C(61)-C(62)	1.542(3)
C(61)-H(61A)	1.0000

C(62)-C(63)	1.534(3)
C(62)-H(62A)	0.9900
C(62)-H(62B)	0.9900
C(63)-C(64)	1.519(3)
C(63)-H(63A)	0.9900
C(63)-H(63B)	0.9900
C(64)-C(65)	1.518(3)
C(64)-H(64A)	0.9900
C(64)-H(64B)	0.9900
C(65)-C(66)	1.534(3)
C(65)-H(65A)	0.9900
C(65)-H(65B)	0.9900
C(66)-H(66A)	0.9900
C(66)-H(66B)	0.9900
C(70)-C(71)	1.463(3)
C(71)-C(72)	1.391(3)
C(71)-C(76)	1.393(3)
C(72)-C(73)	1.374(3)
C(72)-H(72A)	0.9500
C(73)-C(74)	1.398(3)
C(73)-H(73A)	0.9500
C(74)-C(75)	1.389(3)
C(75)-C(76)	1.378(3)
C(75)-H(75A)	0.9500
C(76)-H(76A)	0.9500
C(77)-H(77A)	0.9800
C(77)-H(77B)	0.9800
C(77)-H(77C)	0.9800
C(80)-C(90)	1.335(3)
C(80)-C(81)	1.468(3)
C(80)-H(80A)	0.9500
C(81)-C(86)	1.393(3)
C(81)-C(82)	1.396(3)
C(82)-C(83)	1.392(3)
C(82)-H(82A)	0.9500
C(83)-C(84)	1.374(4)

C(83)-H(83A)	0.9500
C(84)-C(85)	1.392(4)
C(84)-H(84A)	0.9500
C(85)-C(86)	1.370(4)
C(85)-H(85A)	0.9500
C(86)-H(86A)	0.9500
C(1S)-C(2S)	1.523(4)
C(1S)-H(1SA)	0.9800
C(1S)-H(1SB)	0.9800
C(1S)-H(1SC)	0.9800
C(2S)-C(3S)	1.517(4)
C(2S)-H(2SA)	0.9900
C(2S)-H(2SB)	0.9900
C(3S)-C(4S)	1.512(4)
C(3S)-H(3SA)	0.9900
C(3S)-H(3SB)	0.9900
C(4S)-C(5S)	1.514(4)
C(4S)-H(4SA)	0.9900
C(4S)-H(4SB)	0.9900
C(5S)-C(6S)	1.528(4)
C(5S)-H(5SA)	0.9900
C(5S)-H(5SB)	0.9900
C(6S)-H(6SA)	0.9800
C(6S)-H(6SB)	0.9800
C(6S)-H(6SC)	0.9800
C(10)-Ru(1)-C(90)	91.93(9)
C(10)-Ru(1)-O(1)	170.64(7)
C(90)-Ru(1)-O(1)	78.71(7)
C(10)-Ru(1)-P(2)	90.35(7)
C(90)-Ru(1)-P(2)	93.85(6)
O(1)-Ru(1)-P(2)	90.60(4)
C(10)-Ru(1)-P(1)	90.33(7)
C(90)-Ru(1)-P(1)	92.76(6)
O(1)-Ru(1)-P(1)	89.81(4)
P(2)-Ru(1)-P(1)	173.331(18)

C(10)-Ru(1)-Cl(1)	103.16(6)
C(90)-Ru(1)-Cl(1)	164.87(6)
O(1)-Ru(1)-Cl(1)	86.19(4)
P(2)-Ru(1)-Cl(1)	87.287(17)
P(1)-Ru(1)-Cl(1)	86.098(17)
C(21)-P(1)-C(11)	105.34(10)
C(21)-P(1)-C(31)	100.37(9)
C(11)-P(1)-C(31)	104.58(9)
C(21)-P(1)-Ru(1)	119.00(7)
C(11)-P(1)-Ru(1)	112.75(7)
C(31)-P(1)-Ru(1)	113.17(7)
C(41)-P(2)-C(51)	101.70(10)
C(41)-P(2)-C(61)	104.00(10)
C(51)-P(2)-C(61)	104.79(10)
C(41)-P(2)-Ru(1)	119.45(7)
C(51)-P(2)-Ru(1)	112.17(7)
C(61)-P(2)-Ru(1)	113.15(7)
C(70)-O(1)-Ru(1)	113.22(13)
C(70)-O(2)-C(90)	115.70(16)
C(74)-O(3)-C(77)	118.48(18)
O(10)-C(10)-Ru(1)	175.85(18)
C(16)-C(11)-C(12)	108.13(17)
C(16)-C(11)-P(1)	116.09(14)
C(12)-C(11)-P(1)	115.62(14)
C(16)-C(11)-H(11A)	105.3
C(12)-C(11)-H(11A)	105.3
P(1)-C(11)-H(11A)	105.3
C(13)-C(12)-C(11)	109.54(17)
C(13)-C(12)-H(12A)	109.8
C(11)-C(12)-H(12A)	109.8
C(13)-C(12)-H(12B)	109.8
C(11)-C(12)-H(12B)	109.8
H(12A)-C(12)-H(12B)	108.2
C(14)-C(13)-C(12)	112.36(18)
C(14)-C(13)-H(13A)	109.1
C(12)-C(13)-H(13A)	109.1

C(14)-C(13)-H(13B)	109.1
C(12)-C(13)-H(13B)	109.1
H(13A)-C(13)-H(13B)	107.9
C(13)-C(14)-C(15)	111.39(19)
C(13)-C(14)-H(14A)	109.3
C(15)-C(14)-H(14A)	109.3
C(13)-C(14)-H(14B)	109.4
C(15)-C(14)-H(14B)	109.3
H(14A)-C(14)-H(14B)	108.0
C(14)-C(15)-C(16)	111.57(18)
C(14)-C(15)-H(15A)	109.3
C(16)-C(15)-H(15A)	109.3
C(14)-C(15)-H(15B)	109.3
C(16)-C(15)-H(15B)	109.3
H(15A)-C(15)-H(15B)	108.0
C(11)-C(16)-C(15)	110.52(18)
C(11)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16A)	109.5
C(11)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	108.1
C(22)-C(21)-C(26)	110.54(16)
C(22)-C(21)-P(1)	112.85(14)
C(26)-C(21)-P(1)	113.59(14)
C(22)-C(21)-H(21A)	106.4
C(26)-C(21)-H(21A)	106.4
P(1)-C(21)-H(21A)	106.4
C(23)-C(22)-C(21)	110.32(17)
C(23)-C(22)-H(22A)	109.6
C(21)-C(22)-H(22A)	109.6
C(23)-C(22)-H(22B)	109.6
C(21)-C(22)-H(22B)	109.6
H(22A)-C(22)-H(22B)	108.1
C(24)-C(23)-C(22)	111.57(19)
C(24)-C(23)-H(23A)	109.3
C(22)-C(23)-H(23A)	109.3

C(24)-C(23)-H(23B)	109.3
C(22)-C(23)-H(23B)	109.3
H(23A)-C(23)-H(23B)	108.0
C(23)-C(24)-C(25)	111.18(18)
C(23)-C(24)-H(24A)	109.4
C(25)-C(24)-H(24A)	109.4
C(23)-C(24)-H(24B)	109.4
C(25)-C(24)-H(24B)	109.4
H(24A)-C(24)-H(24B)	108.0
C(24)-C(25)-C(26)	111.38(18)
C(24)-C(25)-H(25A)	109.4
C(26)-C(25)-H(25A)	109.4
C(24)-C(25)-H(25B)	109.4
C(26)-C(25)-H(25B)	109.4
H(25A)-C(25)-H(25B)	108.0
C(25)-C(26)-C(21)	110.42(18)
C(25)-C(26)-H(26A)	109.6
C(21)-C(26)-H(26A)	109.6
C(25)-C(26)-H(26B)	109.6
C(21)-C(26)-H(26B)	109.6
H(26A)-C(26)-H(26B)	108.1
C(32)-C(31)-C(36)	108.86(17)
C(32)-C(31)-P(1)	116.62(15)
C(36)-C(31)-P(1)	114.54(14)
C(32)-C(31)-H(31A)	105.2
C(36)-C(31)-H(31A)	105.2
P(1)-C(31)-H(31A)	105.2
C(33)-C(32)-C(31)	110.91(19)
C(33)-C(32)-H(32A)	109.5
C(31)-C(32)-H(32A)	109.5
C(33)-C(32)-H(32B)	109.5
C(31)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	108.0
C(34)-C(33)-C(32)	110.7(2)
C(34)-C(33)-H(33A)	109.5
C(32)-C(33)-H(33A)	109.5

C(34)-C(33)-H(33B)	109.5
C(32)-C(33)-H(33B)	109.5
H(33A)-C(33)-H(33B)	108.1
C(35)-C(34)-C(33)	111.0(2)
C(35)-C(34)-H(34A)	109.4
C(33)-C(34)-H(34A)	109.4
C(35)-C(34)-H(34B)	109.4
C(33)-C(34)-H(34B)	109.4
H(34A)-C(34)-H(34B)	108.0
C(34)-C(35)-C(36)	112.1(2)
C(34)-C(35)-H(35A)	109.2
C(36)-C(35)-H(35A)	109.2
C(34)-C(35)-H(35B)	109.2
C(36)-C(35)-H(35B)	109.2
H(35A)-C(35)-H(35B)	107.9
C(31)-C(36)-C(35)	110.20(18)
C(31)-C(36)-H(36A)	109.6
C(35)-C(36)-H(36A)	109.6
C(31)-C(36)-H(36B)	109.6
C(35)-C(36)-H(36B)	109.6
H(36A)-C(36)-H(36B)	108.1
C(46)-C(41)-C(42)	110.56(17)
C(46)-C(41)-P(2)	112.55(15)
C(42)-C(41)-P(2)	114.67(15)
C(46)-C(41)-H(41A)	106.1
C(42)-C(41)-H(41A)	106.1
P(2)-C(41)-H(41A)	106.1
C(41)-C(42)-C(43)	109.84(18)
C(41)-C(42)-H(42A)	109.7
C(43)-C(42)-H(42A)	109.7
C(41)-C(42)-H(42B)	109.7
C(43)-C(42)-H(42B)	109.7
H(42A)-C(42)-H(42B)	108.2
C(44)-C(43)-C(42)	111.3(2)
C(44)-C(43)-H(43A)	109.4
C(42)-C(43)-H(43A)	109.4

C(44)-C(43)-H(43B)	109.4
C(42)-C(43)-H(43B)	109.4
H(43A)-C(43)-H(43B)	108.0
C(45)-C(44)-C(43)	111.5(2)
C(45)-C(44)-H(44A)	109.3
C(43)-C(44)-H(44A)	109.3
C(45)-C(44)-H(44B)	109.3
C(43)-C(44)-H(44B)	109.3
H(44A)-C(44)-H(44B)	108.0
C(44)-C(45)-C(46)	111.37(19)
C(44)-C(45)-H(45A)	109.4
C(46)-C(45)-H(45A)	109.4
C(44)-C(45)-H(45B)	109.4
C(46)-C(45)-H(45B)	109.4
H(45A)-C(45)-H(45B)	108.0
C(41)-C(46)-C(45)	110.38(19)
C(41)-C(46)-H(46A)	109.6
C(45)-C(46)-H(46A)	109.6
C(41)-C(46)-H(46B)	109.6
C(45)-C(46)-H(46B)	109.6
H(46A)-C(46)-H(46B)	108.1
C(52)-C(51)-C(56)	108.45(17)
C(52)-C(51)-P(2)	117.16(15)
C(56)-C(51)-P(2)	113.99(14)
C(52)-C(51)-H(51A)	105.4
C(56)-C(51)-H(51A)	105.4
P(2)-C(51)-H(51A)	105.4
C(53)-C(52)-C(51)	110.54(19)
C(53)-C(52)-H(52A)	109.5
C(51)-C(52)-H(52A)	109.5
C(53)-C(52)-H(52B)	109.5
C(51)-C(52)-H(52B)	109.5
H(52A)-C(52)-H(52B)	108.1
C(54)-C(53)-C(52)	111.24(18)
C(54)-C(53)-H(53A)	109.4
C(52)-C(53)-H(53A)	109.4

C(54)-C(53)-H(53B)	109.4
C(52)-C(53)-H(53B)	109.4
H(53A)-C(53)-H(53B)	108.0
C(55)-C(54)-C(53)	111.24(19)
C(55)-C(54)-H(54A)	109.4
C(53)-C(54)-H(54A)	109.4
C(55)-C(54)-H(54B)	109.4
C(53)-C(54)-H(54B)	109.4
H(54A)-C(54)-H(54B)	108.0
C(54)-C(55)-C(56)	111.83(18)
C(54)-C(55)-H(55A)	109.3
C(56)-C(55)-H(55A)	109.3
C(54)-C(55)-H(55B)	109.2
C(56)-C(55)-H(55B)	109.3
H(55A)-C(55)-H(55B)	107.9
C(55)-C(56)-C(51)	110.41(17)
C(55)-C(56)-H(56A)	109.6
C(51)-C(56)-H(56A)	109.6
C(55)-C(56)-H(56B)	109.6
C(51)-C(56)-H(56B)	109.6
H(56A)-C(56)-H(56B)	108.1
C(66)-C(61)-C(62)	108.69(17)
C(66)-C(61)-P(2)	115.22(15)
C(62)-C(61)-P(2)	115.45(15)
C(66)-C(61)-H(61A)	105.5
C(62)-C(61)-H(61A)	105.5
P(2)-C(61)-H(61A)	105.5
C(63)-C(62)-C(61)	110.01(18)
C(63)-C(62)-H(62A)	109.7
C(61)-C(62)-H(62A)	109.7
C(63)-C(62)-H(62B)	109.7
C(61)-C(62)-H(62B)	109.7
H(62A)-C(62)-H(62B)	108.2
C(64)-C(63)-C(62)	112.06(19)
C(64)-C(63)-H(63A)	109.2
C(62)-C(63)-H(63A)	109.2

C(64)-C(63)-H(63B)	109.2
C(62)-C(63)-H(63B)	109.2
H(63A)-C(63)-H(63B)	107.9
C(65)-C(64)-C(63)	110.87(19)
C(65)-C(64)-H(64A)	109.5
C(63)-C(64)-H(64A)	109.5
C(65)-C(64)-H(64B)	109.5
C(63)-C(64)-H(64B)	109.5
H(64A)-C(64)-H(64B)	108.1
C(64)-C(65)-C(66)	112.00(19)
C(64)-C(65)-H(65A)	109.2
C(66)-C(65)-H(65A)	109.2
C(64)-C(65)-H(65B)	109.2
C(66)-C(65)-H(65B)	109.2
H(65A)-C(65)-H(65B)	107.9
C(61)-C(66)-C(65)	111.08(18)
C(61)-C(66)-H(66A)	109.4
C(65)-C(66)-H(66A)	109.4
C(61)-C(66)-H(66B)	109.4
C(65)-C(66)-H(66B)	109.4
H(66A)-C(66)-H(66B)	108.0
O(1)-C(70)-O(2)	121.80(19)
O(1)-C(70)-C(71)	120.77(18)
O(2)-C(70)-C(71)	117.42(18)
C(72)-C(71)-C(76)	118.9(2)
C(72)-C(71)-C(70)	123.42(19)
C(76)-C(71)-C(70)	117.70(19)
C(73)-C(72)-C(71)	120.3(2)
C(73)-C(72)-H(72A)	119.8
C(71)-C(72)-H(72A)	119.8
C(72)-C(73)-C(74)	120.2(2)
C(72)-C(73)-H(73A)	119.9
C(74)-C(73)-H(73A)	119.9
O(3)-C(74)-C(75)	124.1(2)
O(3)-C(74)-C(73)	115.7(2)
C(75)-C(74)-C(73)	120.2(2)

C(76)-C(75)-C(74)	118.9(2)
C(76)-C(75)-H(75A)	120.5
C(74)-C(75)-H(75A)	120.5
C(75)-C(76)-C(71)	121.5(2)
C(75)-C(76)-H(76A)	119.2
C(71)-C(76)-H(76A)	119.2
O(3)-C(77)-H(77A)	109.5
O(3)-C(77)-H(77B)	109.5
H(77A)-C(77)-H(77B)	109.5
O(3)-C(77)-H(77C)	109.5
H(77A)-C(77)-H(77C)	109.5
H(77B)-C(77)-H(77C)	109.5
C(90)-C(80)-C(81)	134.8(2)
C(90)-C(80)-H(80A)	112.6
C(81)-C(80)-H(80A)	112.6
C(86)-C(81)-C(82)	116.8(2)
C(86)-C(81)-C(80)	117.3(2)
C(82)-C(81)-C(80)	125.83(19)
C(83)-C(82)-C(81)	121.3(2)
C(83)-C(82)-H(82A)	119.3
C(81)-C(82)-H(82A)	119.3
C(84)-C(83)-C(82)	120.4(2)
C(84)-C(83)-H(83A)	119.8
C(82)-C(83)-H(83A)	119.8
C(83)-C(84)-C(85)	119.1(2)
C(83)-C(84)-H(84A)	120.5
C(85)-C(84)-H(84A)	120.5
C(86)-C(85)-C(84)	120.2(2)
C(86)-C(85)-H(85A)	119.9
C(84)-C(85)-H(85A)	119.9
C(85)-C(86)-C(81)	122.2(2)
C(85)-C(86)-H(86A)	118.9
C(81)-C(86)-H(86A)	118.9
C(80)-C(90)-O(2)	113.30(18)
C(80)-C(90)-Ru(1)	136.18(17)
O(2)-C(90)-Ru(1)	110.50(13)

C(2S)-C(1S)-H(1SA)	109.5
C(2S)-C(1S)-H(1SB)	109.5
H(1SA)-C(1S)-H(1SB)	109.5
C(2S)-C(1S)-H(1SC)	109.5
H(1SA)-C(1S)-H(1SC)	109.5
H(1SB)-C(1S)-H(1SC)	109.5
C(3S)-C(2S)-C(1S)	113.6(2)
C(3S)-C(2S)-H(2SA)	108.8
C(1S)-C(2S)-H(2SA)	108.8
C(3S)-C(2S)-H(2SB)	108.8
C(1S)-C(2S)-H(2SB)	108.8
H(2SA)-C(2S)-H(2SB)	107.7
C(4S)-C(3S)-C(2S)	115.6(2)
C(4S)-C(3S)-H(3SA)	108.4
C(2S)-C(3S)-H(3SA)	108.4
C(4S)-C(3S)-H(3SB)	108.4
C(2S)-C(3S)-H(3SB)	108.4
H(3SA)-C(3S)-H(3SB)	107.4
C(3S)-C(4S)-C(5S)	114.5(2)
C(3S)-C(4S)-H(4SA)	108.6
C(5S)-C(4S)-H(4SA)	108.6
C(3S)-C(4S)-H(4SB)	108.6
C(5S)-C(4S)-H(4SB)	108.6
H(4SA)-C(4S)-H(4SB)	107.6
C(4S)-C(5S)-C(6S)	114.2(3)
C(4S)-C(5S)-H(5SA)	108.7
C(6S)-C(5S)-H(5SA)	108.7
C(4S)-C(5S)-H(5SB)	108.7
C(6S)-C(5S)-H(5SB)	108.7
H(5SA)-C(5S)-H(5SB)	107.6
C(5S)-C(6S)-H(6SA)	109.5
C(5S)-C(6S)-H(6SB)	109.5
H(6SA)-C(6S)-H(6SB)	109.5
C(5S)-C(6S)-H(6SC)	109.5
H(6SA)-C(6S)-H(6SC)	109.5
H(6SB)-C(6S)-H(6SC)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S10. Anisotropic displacement parameters ($Å^2$x 10^3) for **7**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	14(1)	20(1)	14(1)	4(1)	5(1)	7(1)
Cl(1)	21(1)	26(1)	20(1)	6(1)	10(1)	10(1)
P(1)	16(1)	20(1)	16(1)	6(1)	5(1)	8(1)
P(2)	17(1)	20(1)	16(1)	5(1)	6(1)	6(1)
O(1)	16(1)	26(1)	17(1)	4(1)	4(1)	7(1)
O(2)	18(1)	27(1)	16(1)	4(1)	4(1)	7(1)
O(3)	25(1)	75(1)	21(1)	0(1)	2(1)	25(1)
O(10)	24(1)	30(1)	19(1)	5(1)	2(1)	10(1)
C(10)	24(1)	23(1)	20(1)	7(1)	11(1)	11(1)
C(11)	16(1)	23(1)	20(1)	7(1)	7(1)	7(1)
C(12)	18(1)	27(1)	24(1)	9(1)	7(1)	9(1)
C(13)	20(1)	35(1)	28(1)	12(1)	9(1)	13(1)
C(14)	20(1)	36(1)	28(1)	10(1)	10(1)	7(1)
C(15)	24(1)	28(1)	32(1)	11(1)	12(1)	8(1)
C(16)	22(1)	26(1)	27(1)	8(1)	9(1)	10(1)
C(21)	19(1)	21(1)	19(1)	5(1)	7(1)	9(1)
C(22)	21(1)	31(1)	18(1)	6(1)	5(1)	13(1)
C(23)	24(1)	32(1)	20(1)	2(1)	5(1)	11(1)
C(24)	28(1)	39(1)	24(1)	3(1)	9(1)	16(1)
C(25)	25(1)	32(1)	25(1)	7(1)	10(1)	15(1)
C(26)	20(1)	28(1)	22(1)	6(1)	5(1)	10(1)
C(31)	18(1)	28(1)	18(1)	8(1)	4(1)	9(1)
C(32)	32(1)	30(1)	24(1)	10(1)	4(1)	14(1)
C(33)	42(2)	39(2)	31(1)	15(1)	2(1)	21(1)
C(34)	44(2)	44(2)	24(1)	12(1)	-1(1)	19(1)
C(35)	31(1)	40(1)	20(1)	6(1)	3(1)	13(1)
C(36)	26(1)	33(1)	18(1)	9(1)	7(1)	13(1)
C(41)	23(1)	27(1)	18(1)	10(1)	8(1)	8(1)
C(42)	23(1)	32(1)	23(1)	9(1)	9(1)	7(1)
C(43)	29(1)	39(1)	29(1)	13(1)	14(1)	8(1)
C(44)	37(1)	48(2)	25(1)	14(1)	14(1)	12(1)

C(45)	36(1)	45(2)	19(1)	12(1)	9(1)	14(1)
C(46)	24(1)	33(1)	20(1)	8(1)	8(1)	10(1)
C(51)	18(1)	23(1)	19(1)	5(1)	5(1)	4(1)
C(52)	26(1)	26(1)	22(1)	6(1)	8(1)	4(1)
C(53)	26(1)	27(1)	30(1)	4(1)	7(1)	-1(1)
C(54)	26(1)	30(1)	24(1)	3(1)	2(1)	5(1)
C(55)	27(1)	32(1)	20(1)	5(1)	3(1)	9(1)
C(56)	22(1)	24(1)	20(1)	4(1)	6(1)	5(1)
C(61)	21(1)	23(1)	21(1)	6(1)	6(1)	10(1)
C(62)	22(1)	24(1)	26(1)	7(1)	6(1)	10(1)
C(63)	23(1)	30(1)	32(1)	8(1)	8(1)	11(1)
C(64)	29(1)	34(1)	34(1)	9(1)	7(1)	18(1)
C(65)	34(1)	26(1)	34(1)	11(1)	10(1)	15(1)
C(66)	26(1)	24(1)	26(1)	8(1)	6(1)	9(1)
C(70)	22(1)	18(1)	20(1)	6(1)	6(1)	6(1)
C(71)	20(1)	20(1)	22(1)	7(1)	6(1)	7(1)
C(72)	26(1)	34(1)	18(1)	5(1)	8(1)	12(1)
C(73)	20(1)	49(2)	24(1)	5(1)	8(1)	17(1)
C(74)	21(1)	34(1)	24(1)	6(1)	4(1)	11(1)
C(75)	25(1)	26(1)	20(1)	6(1)	8(1)	10(1)
C(76)	19(1)	29(1)	24(1)	8(1)	9(1)	10(1)
C(77)	31(1)	56(2)	20(1)	4(1)	5(1)	20(1)
C(80)	17(1)	24(1)	21(1)	6(1)	4(1)	8(1)
C(81)	22(1)	22(1)	23(1)	7(1)	10(1)	6(1)
C(82)	28(1)	36(1)	22(1)	5(1)	8(1)	16(1)
C(83)	28(1)	46(2)	33(1)	11(1)	10(1)	20(1)
C(84)	33(1)	50(2)	37(1)	8(1)	23(1)	18(1)
C(85)	40(2)	75(2)	21(1)	1(1)	11(1)	14(1)
C(86)	25(1)	58(2)	26(1)	6(1)	6(1)	12(1)
C(90)	17(1)	22(1)	22(1)	7(1)	5(1)	7(1)
C(1S)	54(2)	39(2)	42(2)	8(1)	15(1)	8(1)
C(2S)	57(2)	54(2)	44(2)	12(1)	23(1)	22(2)
C(3S)	48(2)	43(2)	43(2)	16(1)	24(1)	20(1)
C(4S)	50(2)	56(2)	52(2)	28(2)	29(1)	25(2)
C(5S)	47(2)	69(2)	51(2)	27(2)	20(1)	22(2)
C(6S)	55(2)	90(3)	68(2)	38(2)	22(2)	34(2)

Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **7**.

	x	y	z	U(eq)
H(11A)	11039	3913	7145	23
H(12A)	12205	4292	8467	27
H(12B)	11661	3065	7949	27
H(13A)	13961	3938	8054	31
H(13B)	13167	3714	7336	31
H(14A)	14717	5535	7655	33
H(14B)	14240	5856	8303	33
H(15A)	12779	5492	7028	33
H(15B)	13351	6671	7586	33
H(16A)	11835	5942	8177	29
H(16B)	11045	5808	7472	29
H(21A)	9556	5607	8171	23
H(22A)	9450	4365	9101	27
H(22B)	10783	5135	8979	27
H(23A)	10218	6163	9874	31
H(23B)	10254	6781	9318	31
H(24A)	8349	6731	9691	36
H(24B)	7911	5386	9567	36
H(25A)	8000	6520	8581	31
H(25B)	6687	5745	8716	31
H(26A)	7242	4724	7810	28
H(26B)	7222	4103	8366	28
H(31A)	7387	3504	6954	25
H(32A)	8518	5495	7234	33
H(32B)	9422	5274	6748	33
H(33A)	6620	4674	6373	43
H(33B)	7663	5701	6226	43
H(34A)	6774	4068	5306	44
H(34B)	8337	4432	5531	44
H(35A)	7416	2468	5329	37
H(35B)	6453	2610	5794	37
H(36A)	8210	2224	6345	29

H(36B)	9261	3269	6216	29
H(41A)	7603	-1273	8526	27
H(42A)	5597	-1053	8125	31
H(42B)	6119	212	8599	31
H(43A)	4811	-1028	9086	38
H(43B)	5697	-1811	9010	38
H(44A)	6558	464	9843	43
H(44B)	6332	-653	10078	43
H(45A)	8124	-954	9712	39
H(45B)	8608	315	10177	39
H(46A)	8508	1045	9282	30
H(46B)	9414	278	9220	30
H(51A)	6142	-914	7169	25
H(52A)	7170	-2703	7132	31
H(52B)	6251	-2428	7599	31
H(53A)	4960	-3903	6645	37
H(53B)	4508	-2823	6702	37
H(54A)	6148	-3418	5891	35
H(54B)	4682	-3457	5645	35
H(55A)	5348	-1484	5997	33
H(55B)	6273	-1813	5548	33
H(56A)	7554	-319	6496	27
H(56B)	7973	-1413	6462	27
H(61A)	9700	-815	7410	25
H(62A)	11098	1047	8038	29
H(62B)	11116	624	8671	29
H(63A)	12084	-250	7594	34
H(63B)	12996	547	8282	34
H(64A)	12750	-1395	8157	37
H(64B)	12239	-889	8762	37
H(65A)	10674	-2657	8188	36
H(65B)	10612	-2313	7532	36
H(66A)	8754	-2194	7917	30
H(66B)	9668	-1360	8596	30
H(72A)	3667	1492	7293	31
H(73A)	1769	930	6491	36

H(75A)	3688	-33	5150	28
H(76A)	5581	534	5960	28
H(77A)	440	-564	4395	54
H(77B)	1564	-1059	4591	54
H(77C)	1951	189	4505	54
H(80A)	8019	2594	9175	25
H(82A)	4768	2472	8418	34
H(83A)	3317	2972	8994	40
H(84A)	3902	3579	10112	46
H(85A)	5925	3600	10654	58
H(86A)	7329	3052	10085	45
H(1SA)	3841	3875	6285	71
H(1SB)	4041	4006	5596	71
H(1SC)	3537	2772	5697	71
H(2SA)	1558	3033	5872	60
H(2SB)	2062	4260	5763	60
H(3SA)	2045	3368	4680	50
H(3SB)	1428	2163	4798	50
H(4SA)	137	3774	4813	57
H(4SB)	-481	2574	4938	57
H(5SA)	-549	1640	3874	63
H(5SB)	87	2836	3747	63
H(6SA)	-2178	2144	3300	98
H(6SB)	-1838	3264	3882	98
H(6SC)	-2477	2040	3978	98

Table S12. Torsion angles [°] for **7**.

C(10)-Ru(1)-P(1)-C(21)	-61.89(10)
C(90)-Ru(1)-P(1)-C(21)	30.06(10)
O(1)-Ru(1)-P(1)-C(21)	108.75(8)
P(2)-Ru(1)-P(1)-C(21)	-157.68(16)
Cl(1)-Ru(1)-P(1)-C(21)	-165.05(8)
C(10)-Ru(1)-P(1)-C(11)	62.20(9)
C(90)-Ru(1)-P(1)-C(11)	154.15(9)
O(1)-Ru(1)-P(1)-C(11)	-127.16(8)
P(2)-Ru(1)-P(1)-C(11)	-33.59(18)
Cl(1)-Ru(1)-P(1)-C(11)	-40.97(7)
C(10)-Ru(1)-P(1)-C(31)	-179.34(10)
C(90)-Ru(1)-P(1)-C(31)	-87.40(9)
O(1)-Ru(1)-P(1)-C(31)	-8.70(8)
P(2)-Ru(1)-P(1)-C(31)	84.86(17)
Cl(1)-Ru(1)-P(1)-C(31)	77.49(7)
C(10)-Ru(1)-P(2)-C(41)	61.78(10)
C(90)-Ru(1)-P(2)-C(41)	-30.18(10)
O(1)-Ru(1)-P(2)-C(41)	-108.90(9)
P(1)-Ru(1)-P(2)-C(41)	157.57(16)
Cl(1)-Ru(1)-P(2)-C(41)	164.94(8)
C(10)-Ru(1)-P(2)-C(51)	-179.43(9)
C(90)-Ru(1)-P(2)-C(51)	88.61(9)
O(1)-Ru(1)-P(2)-C(51)	9.88(8)
P(1)-Ru(1)-P(2)-C(51)	-83.64(17)
Cl(1)-Ru(1)-P(2)-C(51)	-76.28(7)
C(10)-Ru(1)-P(2)-C(61)	-61.14(10)
C(90)-Ru(1)-P(2)-C(61)	-153.10(9)
O(1)-Ru(1)-P(2)-C(61)	128.17(8)
P(1)-Ru(1)-P(2)-C(61)	34.65(18)
Cl(1)-Ru(1)-P(2)-C(61)	42.01(7)
C(10)-Ru(1)-O(1)-C(70)	-0.3(5)
C(90)-Ru(1)-O(1)-C(70)	1.67(14)
P(2)-Ru(1)-O(1)-C(70)	95.48(14)
P(1)-Ru(1)-O(1)-C(70)	-91.18(14)

Cl(1)-Ru(1)-O(1)-C(70)	-177.28(14)
C(90)-Ru(1)-C(10)-O(10)	0(3)
O(1)-Ru(1)-C(10)-O(10)	2(3)
P(2)-Ru(1)-C(10)-O(10)	-94(3)
P(1)-Ru(1)-C(10)-O(10)	92(3)
Cl(1)-Ru(1)-C(10)-O(10)	178(100)
C(21)-P(1)-C(11)-C(16)	-31.10(17)
C(31)-P(1)-C(11)-C(16)	74.21(17)
Ru(1)-P(1)-C(11)-C(16)	-162.42(13)
C(21)-P(1)-C(11)-C(12)	97.15(16)
C(31)-P(1)-C(11)-C(12)	-157.54(15)
Ru(1)-P(1)-C(11)-C(12)	-34.17(17)
C(16)-C(11)-C(12)-C(13)	-60.6(2)
P(1)-C(11)-C(12)-C(13)	167.34(15)
C(11)-C(12)-C(13)-C(14)	57.6(2)
C(12)-C(13)-C(14)-C(15)	-53.0(2)
C(13)-C(14)-C(15)-C(16)	52.3(3)
C(12)-C(11)-C(16)-C(15)	60.9(2)
P(1)-C(11)-C(16)-C(15)	-167.25(15)
C(14)-C(15)-C(16)-C(11)	-57.2(2)
C(11)-P(1)-C(21)-C(22)	-71.97(17)
C(31)-P(1)-C(21)-C(22)	179.63(15)
Ru(1)-P(1)-C(21)-C(22)	55.66(17)
C(11)-P(1)-C(21)-C(26)	161.20(15)
C(31)-P(1)-C(21)-C(26)	52.80(17)
Ru(1)-P(1)-C(21)-C(26)	-71.17(16)
C(26)-C(21)-C(22)-C(23)	-57.3(2)
P(1)-C(21)-C(22)-C(23)	174.22(15)
C(21)-C(22)-C(23)-C(24)	56.7(2)
C(22)-C(23)-C(24)-C(25)	-55.5(3)
C(23)-C(24)-C(25)-C(26)	55.1(3)
C(24)-C(25)-C(26)-C(21)	-56.0(2)
C(22)-C(21)-C(26)-C(25)	57.1(2)
P(1)-C(21)-C(26)-C(25)	-174.84(15)
C(21)-P(1)-C(31)-C(32)	45.26(18)
C(11)-P(1)-C(31)-C(32)	-63.74(18)

Ru(1)-P(1)-C(31)-C(32)	173.17(14)
C(21)-P(1)-C(31)-C(36)	174.04(16)
C(11)-P(1)-C(31)-C(36)	65.04(18)
Ru(1)-P(1)-C(31)-C(36)	-58.05(17)
C(36)-C(31)-C(32)-C(33)	59.6(2)
P(1)-C(31)-C(32)-C(33)	-168.89(16)
C(31)-C(32)-C(33)-C(34)	-58.5(3)
C(32)-C(33)-C(34)-C(35)	55.2(3)
C(33)-C(34)-C(35)-C(36)	-54.6(3)
C(32)-C(31)-C(36)-C(35)	-57.8(2)
P(1)-C(31)-C(36)-C(35)	169.65(16)
C(34)-C(35)-C(36)-C(31)	56.3(3)
C(51)-P(2)-C(41)-C(46)	179.69(16)
C(61)-P(2)-C(41)-C(46)	71.01(17)
Ru(1)-P(2)-C(41)-C(46)	-56.30(17)
C(51)-P(2)-C(41)-C(42)	-52.78(18)
C(61)-P(2)-C(41)-C(42)	-161.47(16)
Ru(1)-P(2)-C(41)-C(42)	71.23(17)
C(46)-C(41)-C(42)-C(43)	-58.1(2)
P(2)-C(41)-C(42)-C(43)	173.40(16)
C(41)-C(42)-C(43)-C(44)	56.6(3)
C(42)-C(43)-C(44)-C(45)	-55.4(3)
C(43)-C(44)-C(45)-C(46)	54.9(3)
C(42)-C(41)-C(46)-C(45)	57.8(2)
P(2)-C(41)-C(46)-C(45)	-172.48(16)
C(44)-C(45)-C(46)-C(41)	-56.1(3)
C(41)-P(2)-C(51)-C(52)	-45.77(18)
C(61)-P(2)-C(51)-C(52)	62.31(18)
Ru(1)-P(2)-C(51)-C(52)	-174.56(14)
C(41)-P(2)-C(51)-C(56)	-173.91(16)
C(61)-P(2)-C(51)-C(56)	-65.83(17)
Ru(1)-P(2)-C(51)-C(56)	57.30(17)
C(56)-C(51)-C(52)-C(53)	-59.5(2)
P(2)-C(51)-C(52)-C(53)	169.79(15)
C(51)-C(52)-C(53)-C(54)	57.8(3)
C(52)-C(53)-C(54)-C(55)	-54.4(3)

C(53)-C(54)-C(55)-C(56)	54.3(3)
C(54)-C(55)-C(56)-C(51)	-57.1(2)
C(52)-C(51)-C(56)-C(55)	58.9(2)
P(2)-C(51)-C(56)-C(55)	-168.59(15)
C(41)-P(2)-C(61)-C(66)	29.60(18)
C(51)-P(2)-C(61)-C(66)	-76.78(17)
Ru(1)-P(2)-C(61)-C(66)	160.72(13)
C(41)-P(2)-C(61)-C(62)	-98.45(17)
C(51)-P(2)-C(61)-C(62)	155.17(15)
Ru(1)-P(2)-C(61)-C(62)	32.67(17)
C(66)-C(61)-C(62)-C(63)	58.9(2)
P(2)-C(61)-C(62)-C(63)	-169.90(15)
C(61)-C(62)-C(63)-C(64)	-57.9(2)
C(62)-C(63)-C(64)-C(65)	54.5(3)
C(63)-C(64)-C(65)-C(66)	-53.3(3)
C(62)-C(61)-C(66)-C(65)	-58.4(2)
P(2)-C(61)-C(66)-C(65)	170.27(15)
C(64)-C(65)-C(66)-C(61)	56.4(3)
Ru(1)-O(1)-C(70)-O(2)	-0.6(2)
Ru(1)-O(1)-C(70)-C(71)	178.76(15)
C(90)-O(2)-C(70)-O(1)	-1.5(3)
C(90)-O(2)-C(70)-C(71)	179.18(17)
O(1)-C(70)-C(71)-C(72)	-178.4(2)
O(2)-C(70)-C(71)-C(72)	1.0(3)
O(1)-C(70)-C(71)-C(76)	2.1(3)
O(2)-C(70)-C(71)-C(76)	-178.54(19)
C(76)-C(71)-C(72)-C(73)	0.5(3)
C(70)-C(71)-C(72)-C(73)	-179.0(2)
C(71)-C(72)-C(73)-C(74)	0.0(4)
C(77)-O(3)-C(74)-C(75)	-0.6(4)
C(77)-O(3)-C(74)-C(73)	179.0(2)
C(72)-C(73)-C(74)-O(3)	179.9(2)
C(72)-C(73)-C(74)-C(75)	-0.5(4)
O(3)-C(74)-C(75)-C(76)	-179.9(2)
C(73)-C(74)-C(75)-C(76)	0.5(4)
C(74)-C(75)-C(76)-C(71)	0.0(3)

C(72)-C(71)-C(76)-C(75)	-0.5(3)
C(70)-C(71)-C(76)-C(75)	179.0(2)
C(90)-C(80)-C(81)-C(86)	176.5(3)
C(90)-C(80)-C(81)-C(82)	-6.0(4)
C(86)-C(81)-C(82)-C(83)	0.4(4)
C(80)-C(81)-C(82)-C(83)	-177.2(2)
C(81)-C(82)-C(83)-C(84)	1.1(4)
C(82)-C(83)-C(84)-C(85)	-1.6(4)
C(83)-C(84)-C(85)-C(86)	0.5(5)
C(84)-C(85)-C(86)-C(81)	1.0(5)
C(82)-C(81)-C(86)-C(85)	-1.5(4)
C(80)-C(81)-C(86)-C(85)	176.3(3)
C(81)-C(80)-C(90)-O(2)	-4.3(4)
C(81)-C(80)-C(90)-Ru(1)	173.93(18)
C(70)-O(2)-C(90)-C(80)	-178.58(19)
C(70)-O(2)-C(90)-Ru(1)	2.8(2)
C(10)-Ru(1)-C(90)-C(80)	-0.8(2)
O(1)-Ru(1)-C(90)-C(80)	179.6(2)
P(2)-Ru(1)-C(90)-C(80)	89.7(2)
P(1)-Ru(1)-C(90)-C(80)	-91.2(2)
Cl(1)-Ru(1)-C(90)-C(80)	-176.44(14)
C(10)-Ru(1)-C(90)-O(2)	177.46(14)
O(1)-Ru(1)-C(90)-O(2)	-2.22(12)
P(2)-Ru(1)-C(90)-O(2)	-92.06(13)
P(1)-Ru(1)-C(90)-O(2)	87.04(13)
Cl(1)-Ru(1)-C(90)-O(2)	1.8(3)
C(1S)-C(2S)-C(3S)-C(4S)	-175.0(3)
C(2S)-C(3S)-C(4S)-C(5S)	-179.4(3)
C(3S)-C(4S)-C(5S)-C(6S)	-179.2(3)

Symmetry transformations used to generate equivalent atoms: